(54) Title: CATALYSTS

(57) Abstract: The invention describes ligands of formula (I), wherein LIG represents an η^5-ligand substituted by a group R_1 and a group $(R'')_m$; X represents a 1 to 3 atom bridge; Y represents a nitrogen or phosphorus atom; Z represents a carbon, nitrogen or phosphorus atom.

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CATALYSTS

This invention relates to catalysts for olefin
polymerisation, in particular to catalyst compounds
containing metals η-bonded by η^5-ligands, e.g.
cyclopentadienyl ligands and η or σ-bonded by a bicyclic
nitrogen ligand, and their use in olefin polymerisation.

In olefin polymerization, it has long been known to
use as a catalyst system the combination of a
metallocene procatalyst and an alumoxane or boron based
co-catalyst.

By "metallocene" is here meant an η-ligand metal
complex, e.g. an "open sandwich" or "half sandwich"
compound in which the metal is complexed by a single η-
ligand, a "sandwich" compound in which the metal is
complexed by two or more η-ligands, a "handcuff"
compound" in which the metal is complexed by a bridged
bis-η-ligand or a "scorpionate" compound in which the
metal is complexed by an η-ligand linked by a bridge to
a σ-ligand.

Metallocene procatalysts are generally used as part
of a catalyst system which also includes an ionic
cocatalyst or catalyst activator, for example, an
aluminoxane (e.g. methylaluminoxane (MAO),
hexaisobutylaluminoxane and tetraisobutylaluminoxane) or
a boron compound (e.g. a fluoroboron compound such as
triphenylpentafluoroboron or triphentylcarbenium
tetraphenylpentafluoroborate ($(C_6H_5)_3B^+B^-(C_6F_5)_4$))

Alumoxanes are compounds with alternating aluminium
and oxygen atoms generally compounds of formula

$$R_2Al\text{-}(O\text{-}AlR)_p\text{-}O\text{-}AlR_2 \qquad\qquad or$$
$$RAl\text{-}(O\text{-}AlR)_p\text{-}O\text{-}AlR$$
$$\underbrace{\qquad\qquad O \qquad\qquad}$$
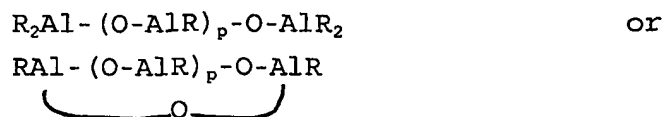
where each R, which may be the same or different, is a

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C_{1-10} alkyl group, and p is an integer having a value between 0 and 40). These compounds may be prepared by reaction of an aluminium alkyl with water. The production and use of alumoxanes is described in the patent literature, especially the patent applications of Texas Alkyls, Albemarle, Ethyl, Phillips, Akzo Nobel, Exxon, Idemitsu Kosan, Witco, BASF and Mitsui.

Traditionally, the most widely used alumoxane is methylalumoxane (MAO), an alumoxane compound in which the R groups are methyls. MAO however is poorly characterised and relatively expensive and efforts have been made to use alumoxanes other than MAO. Thus, for example WO98/32775 (Borealis) proposes the use of metallocene procatalysts with alumoxanes in which R is a C_{2-10} alkyl group, eg hexaisobutylalumoxane (HIBAO). However, such metallocenes generally have poor catalyst activities with non-MAO alumoxanes.

Since each polymerisation catalyst gives rise to polymer products with slightly differing properties, there remains an ongoing search for new and improved olefin polymerisation catalysts.

We have now surprisingly found that a single site procatalyst system based on a η^5-ligand, e.g. cyclopentadienyl type ligand and a η or σ-bonding bicyclic nitrogen ligand may be used very effectively in polymerisation catalysis, especially in the manufacture of polyethylene or polypropylene.

Thus viewed from one aspect the invention provides a compound of formula (I) comprising

                                                        (I)
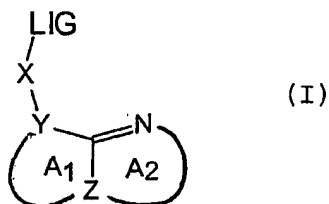
wherein

LIG represents an η^5-ligand substituted by a group R_1 and a group $(R'')_m$;

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X represents a 1 to 3 atom bridge, optionally substituted, e.g. by R'' groups;

Y represents a nitrogen or phosphorus atom;

Z represents a carbon, silicon, nitrogen or phosphorus atom;

the ring denoted by A_1 is an optionally substituted, optionally saturated or unsaturated 5 to 12 membered heterocyclic ring;

the ring denoted by A_2 is an optionally substituted, unsaturated 5 to 12 membered heterocyclic ring;

R_1 represents hydrogen, R'' or a group $OSiR'_3$;

each R', which may be the same or different is a R^+, OR^+, SR^+, NR^+_2 or PR^+_2 group where each R^+ is a C_{1-16} hydrocarbyl group, a tri-C_{1-8}hydrocarbylsilyl group or a tri-C_{1-8}hydrocarbylsiloxy group, preferably R' being a C_{1-12} hydrocarbyl group, e.g. a C_{1-8} alkyl or alkenyl group;

each R'', which may be the same or different is a ring substituent which does not form a σ-bond to a metal η-bonded by the bicyclic ring, eg it may be hydrogen, R^+, OR^+, SR^+, NR^+_2 or PR^+_2 group where each R^+ is a C_{1-16} hydrocarbyl group, a tri-C_{1-8} hydrocarbylsilyl group or a tri-C_{1-8}hydrocarbylsiloxy group; and

m is zero or an integer between 1 and 3.

Viewed from a further aspect the invention provides an olefin polymerisation catalyst system comprising or produced by reaction of (1) a metallated compound as hereinbefore defined (from hereon called a procatalyst) and (2) a cocatalyst, e.g. an aluminium alkyl compound or boron compound, in particular an alumoxane, especially an aluminium alkyl compound comprising alkyl groups containing at least two carbon atoms.

Viewed from a still further aspect the invention provides a process for olefin polymerisation comprising polymerising an olefin in the presence of a catalyst system as hereinbefore described.

Viewed from a yet further aspect the invention

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provides a process for the preparation of a procatalyst,
said process comprising metallating with a group 3 to 7
transition metal a compound of formula (I)

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wherein LIG, X, Y, Z and rings A_1 and A_2 are as
hereinbefore defined.

10   Viewed from a further aspect the invention provides
the use of a procatalyst as hereinbefore defined in
olefin polymerization, especially ethylene or propylene
polymerisation or copolymerisation.

15   Viewed from a yet further aspect the invention
provides an olefin polymer produced by a polymerisation
catalysed by a procatalyst compound as hereinbefore
defined.

20   The compounds of formula (I) as hereinbefore
described may be coupled with a metal from groups 3 to
7. By group 3 (etc) metal is meant a metal in group 3
of the Periodic Table of the Elements, namely Sc, Y,
etc. It is preferable if the metal coupling the

25   compound of the invention is in the III^+ oxidation state,
although metals in the II^+ and IV^+ oxidation states are
also advantageous. The metal employed in the catalyst
system of the invention is most preferably from groups
4, 5 or 6 of the periodic table, e.g. Cr, Mo, W, Ti, Zr,

30   Hf, V, Nb or Ta. Most especially the metal is Cr or Ti,
e.g. Cr^{3+} or Ti^{3+}.

          Where the metal is Cr, it has surprisingly been
found that the catalyst system of the invention is
capable of making polypropylene as a powder.

35   The group 3 to 7 metal in the metallated
procatalyst of the invention coordinates to the η^5-ligand
and σ or η bonds to certain atoms in the bicyclic

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nitrogen ligand. Where the metal forms sigma bonds with
the bicyclic nitrogen ligand, only atoms Z and N can
coordinate to the metal. Thus, the metal may be
coordinated only to atom X, only to N or to both the Z
and N atoms. The Y atom is therefore not involved in
coordination with the metal.

However, if an η ligand is formed between the metal
and bicyclic nitrogen group then coordination to any
double bond present in bicyclic nitrogen ligand is
possible. Such η bonds may be η^2 or η^3 depending on the
nature of the bicyclic nitrogen ligand. The metal may
also be coordinated by hydrogen atoms, hydrocarbyl σ-
ligands (eg optionally substituted C_{1-12} hydrocarbyl
groups, such as C_{1-12} alkyl, alkenyl or alkynyl groups
optionally substituted by fluorine and/or aryl (eg
phenyl) groups), by silane groups (eg $Si(CH_3)_3$), by
halogen atoms (eg chlorine), by C_{1-8}
hydrocarbylheteroatom groups, by tri-C_{1-8}hydrocarbylsilyl
groups, by bridged bis-σ-liganding groups, by amine (eg
$N(CH_3)_2$) or imine (eg N=C or N=P groups, eg $(iPr)_3P=N$)
groups, or by other σ-ligands known for use in
metallocene (pro)catalysts.

By a σ-ligand moiety is meant a group bonded to the
metal at one or more places via a single atom, eg a
hydrogen, halogen, silicon, carbon, oxygen, sulphur or
nitrogen atom.

Examples of σ-ligands include

halogenides (e.g. chloride and fluoride),
hydrogen,
triC_{1-12} hydrocarbyl-silyl or -siloxy(e.g.
trimethylsilyl),
triC_{1-6} hydrocarbylphosphimido (e.g.
triisopropylphosphimido),
C_{1-12} hydrocarbyl or hydrocarbyloxy (e.g. methyl, ethyl,
phenyl, benzyl and methoxy),
diC_{1-6} hydrocarbylamido (e.g. dimethylamido and

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diethylamido), and

5 to 7 ring membered heterocyclyl (eg pyrrolyl, furanyl and pyrrolidinyl). Preferable σ ligands include halogens, alkyls, or chloro-amido groups.

5   Y preferably represents a nitrogen atom.

In the catalyst system formed from the compound of the invention, the Y atom does not sigma coordinate to the metal ion. Instead, the atom at Y serves to provide an atom whereby the bridging group X can join the

10   bicyclic nitrogen group to the η^5-ligand.

The Z atom, which as mentioned above may be involved in coordination with the metal ion, is preferably a phosphorus or nitrogen atom, especially a nitrogen atom.

15   In a most preferred embodiment both Y and Z are nitrogen.

The A rings (A$_1$ and A$_2$), formed partially from the atoms -Y-C-Z- or -N-C-Z- may be of different sizes but are preferably of the same size. Moreover, each ring

20   preferably has either 5 or 6 members. Whilst the rings may contain further heteroatoms selected from N, P, S or B, this is not preferred. Thus, apart from the potential heteroatoms represented by Y and Z, the A rings are preferably formed from carbon atoms. The A

25   rings may contain double bonds and may be aromatic but preferably the rings contain no double bonds in addition to the double bond which must be present between the C and N in formula (I). Preferably, the rings are unsubstitued.

30   Thus suitable bicyclic groups include those illustrated below.

35
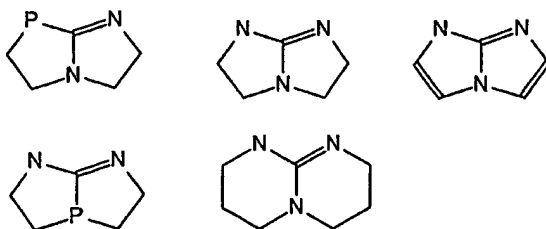
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In a highly preferred embodiment the bicyclic group
is formed from two fused six membered rings and Y and Z
are nitrogen, i.e. the last of the five structures
above.

The η^5-ligand may be any η^5-ligand which forms an η-
bond with the complexing metal ion. Suitable ligands
therefore include dipyridylmethanyl, indenyl, fluorenyl
or cyclopentadienyl ligands. The η^5-ligand is
substituted by groups R_1 and $(R'')_m$ as hereinbefore
defined. Hence, suitable procatalysts of use in the
invention include those of formula
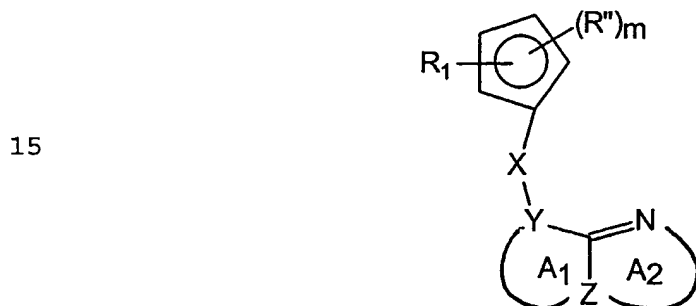
wherein R_1, R'', m, X, Y, Z and rings A_1 and A_2 are
as hereinbefore defined. Alternatively, the η^5-ligand is
of formula

or
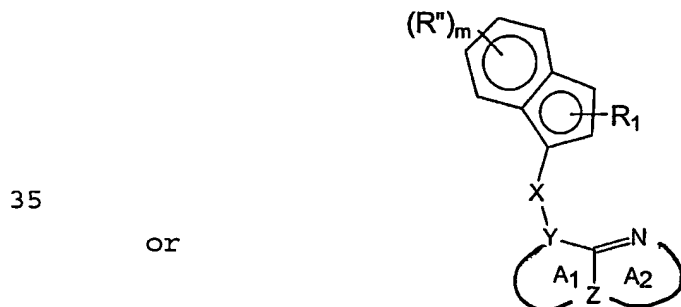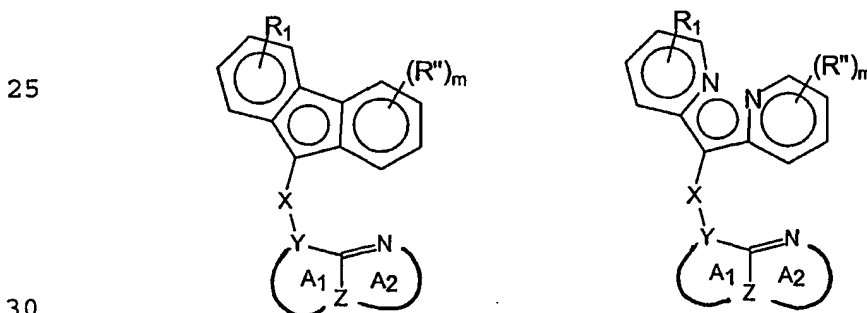
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wherein R_1, R", m, X, Y, Z and rings A_1 and A_2 are as hereinbefore defined. In the above formula, the R_1 and R" groups may be bound to any ring of the η^5-ligand,

5   i.e. although the R_1 group in the formula immediately above is depicted as being generally present on the 5-membered ring, the nomenclature is intended to cover the possibility of the R_1 group being present on the 6-membered ring.

10   The preferred nature of the groups R_1 and R" varies depending on the nature of the η^5-ligand. Where the η^5-ligand is a cyclopentadienyl, R_1 is preferably a group of formula $OSiR'_3$. Preferably R' is a C_{1-12} hydrocarbyl group, e.g. a C_{1-8} alkyl or alkenyl group, especially
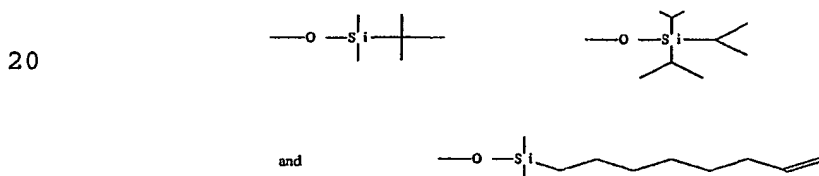
15   methyl or isopropyl.

Examples of suitable R'_3SiO groups in the compounds or procatalysts of the invention include

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Where the η^5-ligand is a cyclopentadienyl group, the

25     $OSiR'_3$ group may be situated at any position on the cyclopentadienyl ring but preferably is alpha to the carbon atom involved in bridging.

The cyclopentadienyl group itself may be substituted by up to three groups R" and R" preferably

30   represents C_{1-6} alkyl, especially methyl. In a highly preferred embodiment, three R" groups are present and R" is methyl. Since R_1 may also represent R" a cyclopentadienyl substituted by four methyl groups is also within the scope of the invention.

35   Also within the scope of the invention are cyclopentadienyl groups wherein one of the carbon atoms not bound to the bridging group X or if present the

OSiR'$_3$ group, is replaced by a heteroatom selected from
phosphorus, silicon, nitrogen or boron. It is stressed
however, that preferably there are no heteratoms present
in the cyclopentadienyl ring.

Thus typical examples of suitable cyclopentadienyl
type moieties include:
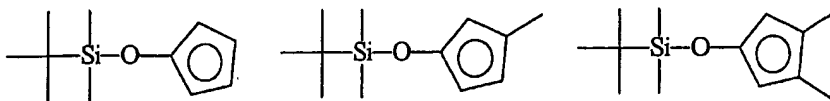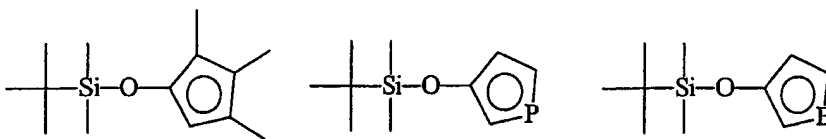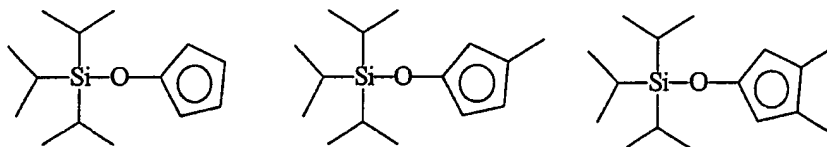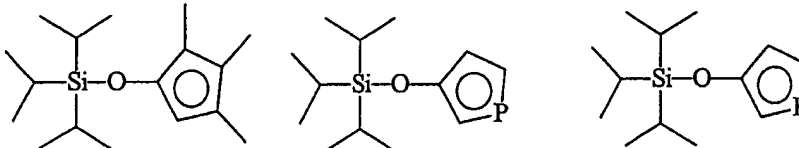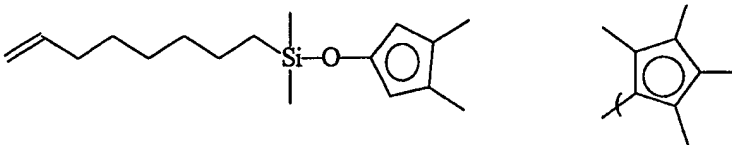
Examples of particular cyclopentadienyl siloxy
groups usable according to the invention include:
triisopropylsiloxycyclopentadienyl,
1-triisopropylsiloxy-3-methyl-cyclopentadienyl,
1-triisopropylsiloxy-3,4-dimethyl-cyclopentadienyl,
1-triisopropylsiloxy-2,3,4-trimethyl-cyclopentadienyl,
(dimethyltertbutylsiloxy)-cyclopentadienyl,

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1-(dimethyltertbutylsiloxy)-3-methylycyclopentadienyl,

1-(dimethyltertbutylsiloxy)- 3,4-
dimethylcyclopentadienyl,

1-(dimethyltertbutylsiloxy)-2,3,4-trimethyl-

5   cyclopentadienyl,

1-triisopropylsiloxy-2-phospholyl,

1-triisopropylsiloxy-3-phospholyl,

1-dimethyltertbutylsiloxy-2-phospholyl,

1-dimethyltertbutylsiloxy-3-phospholyl,

10   1-triisopropylsiloxy-2-borolyl,

1-triisopropylsiloxy-3-borolyl,

1-dimethyltertbutylsiloxy-2-borolyl,

1-dimethyltertbutylsiloxy-3-borolyl,

1-(dimethyloct-1-en-8-ylsiloxy)-3-methyl-

15   cyclopentadienyl,

1-(dimethyloct-1-en-8-ylsiloxy)-3,4-dimethyl-
cyclopentadienyl.

Where the η^5-ligand is a dipyridylmethanyl, indenyl
or fluorenyl species the R_1 may also be a group of

20   formula $OSiR'_3$ as hereinbefore described but preferably
R_1 is hydrogen. R" may represent a C_{1-6} alkyl, especially
methyl but again in a preferred embodiment R" is
hydrogen. Where the η ligand is indenyl, R" may
preferably represent an n-alkenyl, e.g. n-hexyl.

25   Examples of particular further η-ligands are well
known from the technical and patent literature relating
to metallocene olefin polymerization catalysts, e.g. EP-
A-35242 (BASF), EP-A-129368 (Exxon), EP-A-206794
(Exxon), PCT/FI97/00049 (Borealis), EP-A-318048, EP-A-

30   643084, EP-A-69951, EP-A-410734, EP-A-128045, EP-B-35242
(BASF), EP-B-129368 (Exxon), WO97/23493, Organometallics
1995, 14, 471 and EP-B-206794 (Exxon). Further suitable
η-ligands are those of formula

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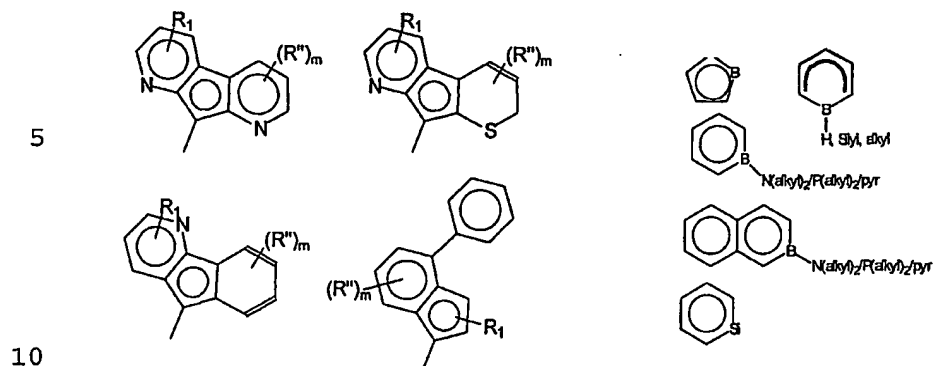
The bridging group X is preferably a one or two atom bridge comprising silicon or carbon. The bridge preferably connects to a carbon atom present in the 5-membered ring of the η^5-ligand. However, where the ligand comprises a heteroatom such as boron, the bridge may attach to the heteroatom or to the heteroatom's substituents. Where the bridge is formed from silicon, the bridge may be of formula -Si(R$_2$)$_2$ wherein each R$_2$ independently represents a C$_{1-10}$ alkyl, C$_{1-10}$ alkenyl, aryl, e.g. phenyl, trimethylsilyl, or both R$_2$ groups taken together may form a ring, e.g. five membered ring, with the Si. Where the bridge comprises carbon, the bridge is preferably a one atom bridge, e.g. -CH$_2$- or -CH(CH$_3$)$_2$-. Suitable bridges are depicted below
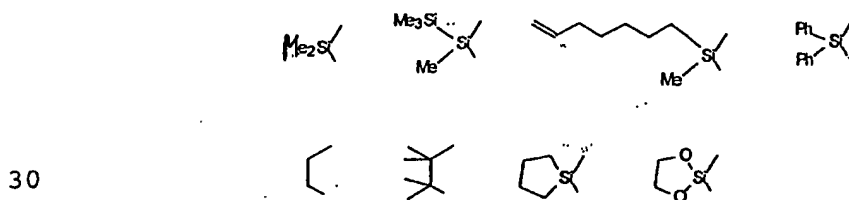
In a highly preferred embodiment, compound according to the invention is of formula

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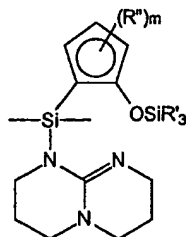
wherein R', m and R" are as hereinbefore described.

Further typical examples of the procatalysts of the invention include:
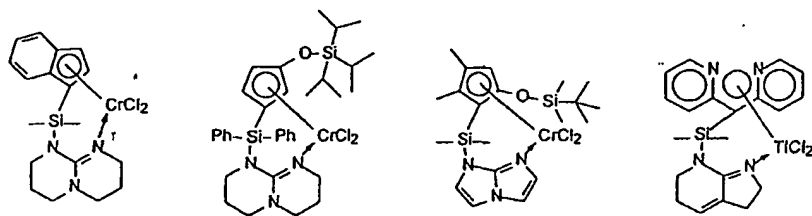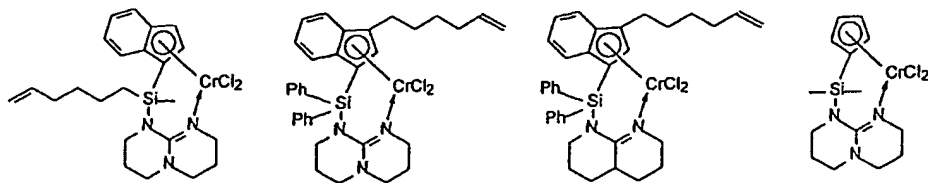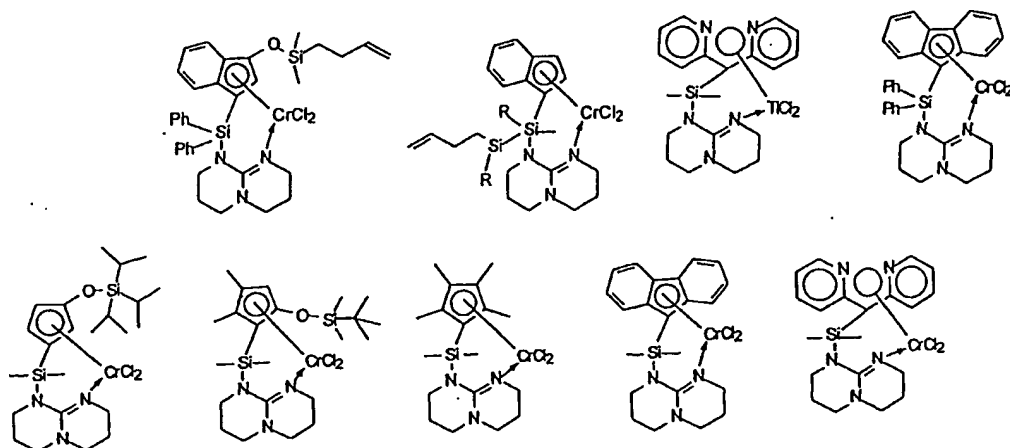
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The procatalysts of the invention may be prepared
by conventional techniques which will be readily devised
by the person skilled in the art. Conveniently for
example, the procatalyst is constructed by combining the
5   bicyclic ligand with, for example, the siloxy
cyclopentadienyl ligand followed by subsequent
metallation. The bridging group may be carried by
either the bicyclic ligand or the cyclopentadienyl
ligand but conveniently the bridging group is attached
10   to the bicyclic group first.
     Where the bicyclic group is for example
1.5.7-triaza[4.4.0]bicyclo-dec-5-ene this may be
deprotonated by a strong base and the resulting anion
reacted with a bridging group such as
15   dimethylsilyldichloride. The cyclopentadienyl η-ligands
used according to the invention may be prepared by
reaction of a corresponding siloxycyclopentadiene with
an organolithium compound, eg methyllithium or
butyllithium. The reaction of the lithium
20   cyclopentadienyl species with the bicyclic ligand
carrying bridiging group gives rise to a compound of the
invention after further deprotonation. These reactions
are depicted in the Scheme below.

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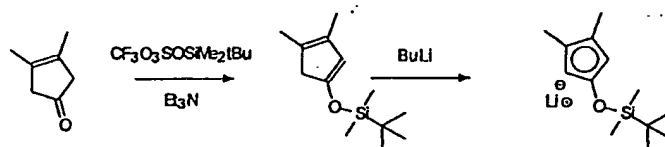
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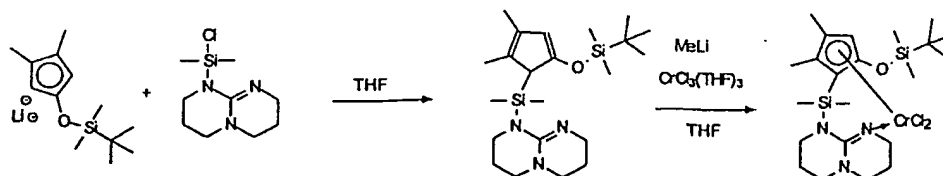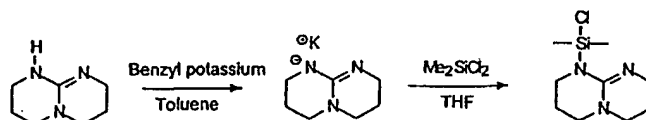
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Fluorenyl and indenyl compounds of the invention may be prepared by analogous techniques to those required to prepare the cyclopentadienyl compounds.

Where the η-ligand is a dipyridylmethanediyl, the
5 bicyclic nitrogen ligand may be reacted with a species generated as illustrated in the following scheme.
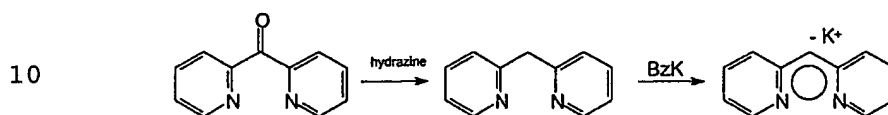
Deprotonation of the product again leaves the
15 compound of the invention. The starting material may be functionalised as necessary to have required substituents using conventional synthetic chemistry. It is of course possible to have the dipyridylmethanediyl carry the bridging group using the following chemistry:

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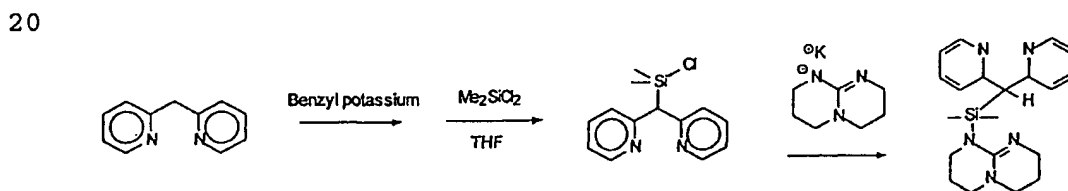
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The compound can be metallated conventionally, eg by reaction with a halide of the metal M, preferably in an organic solvent, eg a hydrocarbon or a hydrocarbon/ether mixture.

30 σ-ligands other than chlorine may be introduced by displacement of chlorine from an η-ligand metal chloride by reaction with appropriate nucleophilic reagent (e.g. methyl lithium or methylmagnesium chloride) or using, instead of a metal halide, a reagent such as
35 tetrakisdimethylamidotitanium or metal compounds with mixed chloro and dimethylamido ligands.

As mentioned above, the olefin polymerisation

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catalyst system of the invention comprises (i) a
procatalyst formed from a metallated compound of formula
(I) and (ii) an aluminium alkyl compound, or the
reaction product thereof. While the aluminium alkyl
compound may be an aluminium trialkyl (eg
triethylaluminium (TEA)) or an aluminium dialkyl halide
(eg diethyl aluminium chloride (DEAC)), it is preferably
an alumoxane, particularly an alumoxane other than MAO,
most preferably an isobutylalumoxane, eg TIBAO
(tetraisobutylalumoxane) or HIBAO
(hexaisobutylalumoxane). Alternatively however the
alkylated (eg methylated) metallocene procatalysts of
the invention (e.g. compounds of formula V wherein Z is
alkyl) may be used with other cocatalysts, eg boron
compounds such as $B(C_6F_5)_3$, $C_6H_5N(CH_3)_2H:B(C_6F_5)_4$,
$(C_6H_5)_3C:B(C_6F_5)_4$ or $Ni(CN)_4[B(C_6F_5)_3]_4{}^{2-}$.

The metallocene procatalyst and cocatalyst may be
introduced into the polymerization reactor separately or
together or, more preferably they are pre-reacted and
their reaction product is introduced into the
polymerization reactor.

If desired the procatalyst, procatalyst/cocatalyst
mixture or a procatalyst/cocatalyst reaction product may
be used in unsupported form or it may be precipitated
and used as such. However the metallocene procatalyst
or its reaction product with the cocatalyst is
preferably introduced into the polymerization reactor in
supported form, eg impregnated into a porous particulate
support.

The particulate support material used is preferably
an organic or inorganic material, e.g. a polymer (such
as for example polyethylene, polypropylene, an ethylene-
propylene copolymer, another polyolefin or polystyrene
or a combination thereof). Such polymeric supports may
be formed by precipitating a polymer or by a
prepolymerization, eg of monomers used in the
polymerization for which the catalyst is intended.

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However, the support is especially preferably a metal or
pseudo metal oxide such as silica, alumina or zirconia
or a mixed oxide such as silica-alumina, in particular
silica, alumina or silica-alumina. Particularly
5   preferably, the support material is acidic, e.g. having
an acidity greater than or equal to silica, more
preferably greater than or equal to silica-alumina and
even more preferably greater than or equal to alumina.
The acidity of the support material can be studied and
10   compared using the TPD (temperature programmed
desorption of gas) method. Generally the gas used will
be ammonia. The more acidic the support, the higher
will be its capacity to adsorb ammonia gas. After being
saturated with ammonia, the sample of support material
15   is heated in a controlled fashion and the quantity of
ammonia desorbed is measured as a function of
temperature.

Especially preferably the support is a porous
material so that the metallocene may be loaded into the
20   pores of the support, e.g. using a process analogous to
those described in WO94/14856 (Mobil), WO95/12622
(Borealis) and WO96/00243 (Exxon). The particle size is
not critical but is preferably in the range 5 to 200 μm,
more preferably 20 to 80 μm.

25   Before loading, the particulate support material is
preferably calcined, ie heat treated, preferably under a
non-reactive gas such as nitrogen. This treatment is
preferably at a temperature in excess of 100°C, more
preferably 200°C or higher, e.g. 200-800°C, particularly
30   about 300°C. The calcination treatment is preferably
effected for several hours, e.g. 2 to 30 hours, more
preferably about 10 hours.

The support may be treated with an alkylating agent
before being loaded with the metallocene. Treatment
35   with the alkylating agent may be effected using an
alkylating agent in a gas or liquid phase, e.g. in an
organic solvent for the alkylating agent. The

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alkylating agent may be any agent capable of introducing alkyl groups, preferably C_{1-6} alkyl groups and most especially preferably methyl groups. Such agents are well known in the field of synthetic organic chemistry.
5   Preferably the alkylating agent is an organometallic compound, especially an organoaluminium compound (such as trimethylaluminium (TMA), dimethyl aluminium chloride, triethylaluminium) or a compound such as methyl lithium, dimethyl magnesium, triethylboron, etc.
10   The quantity of alkylating agent used will depend upon the number of active sites on the surface of the carrier. Thus for example, for a silica support, surface hydroxyls are capable of reacting with the alkylating agent. In general, an excess of alkylating
15   agent is preferably used with any unreacted alkylating agent subsequently being washed away.
      Where an organoaluminium alkylating agent is used, this is preferably used in a quantity sufficient to provide a loading of at least 0.1 mmol Al/g carrier,
20   especially at least 0.5 mmol Al/g, more especially at least 0.7 mmol Al/g, more preferably at least 1.4 mmol Al/g carrier, and still more preferably 2 to 3 mmol Al/g carrier. Where the surface area of the carrier is particularly high, lower aluminium loadings may be used.
25   Thus for example particularly preferred aluminium loadings with a surface area of 300-400 m^2/g carrier may range from 0.5 to 3 mmol Al/g carrier while at surface areas of 700-800 m^2/g carrier the particularly preferred range will be lower.
30   Following treatment of the support material with the alkylating agent, the support is preferably removed from the treatment fluid and any excess treatment fluid is allowed to drain off.
      The optionally alkylated support material is loaded
35   with the procatalyst, preferably using a solution of the procatalyst in an organic solvent therefor, e.g. as described in the patent publications referred to above.

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Preferably, the volume of procatalyst solution used is
from 50 to 500% of the pore volume of the carrier, more
especially preferably 80 to 120%. The concentration of
procatalyst compound in the solution used can vary from
5   dilute to saturated depending on the amount of
metallocene active sites that it is desired be loaded
into the carrier pores.

The active metal (ie. the metal of the procatalyst)
is preferably loaded onto the support material at from
10   0.1 to 4%, preferably 0.5 to 3.0%, especially 1.0 to
2.0%, by weight metal relative to the dry weight of the
support material.

After loading of the procatalyst onto the support
material, the loaded support may be recovered for use in
15   olefin polymerization, e.g. by separation of any excess
procatalyst solution and if desired drying of the loaded
support, optionally at elevated temperatures, e.g. 25 to
80°C.

Alternatively, a cocatalyst, e.g. an alumoxane or
20   an ionic catalyst activator (such as a boron or
aluminium compound, especially a fluoroborate) may also
be mixed with or loaded onto the catalyst support
material. This may be done subsequently or more
preferably simultaneously to loading of the procatalyst,
25   for example by including the cocatalyst in the solution
of the procatalyst or, by contacting the procatalyst
loaded support material with a solution of the
cocatalyst or catalyst activator, e.g. a solution in an
organic solvent. Alternatively however any such further
30   material may be added to the procatalyst loaded support
material in the polymerization reactor or shortly before
dosing of the catalyst material into the reactor.

In this regard, as an alternative to an alumoxane
it may be preferred to use a fluoroborate catalyst
35   activator, especially a $B(C_6F_5)_3$ or more especially a
$^{\ominus}B(C_6F_5)_4$ compound, such as $C_6H_5N(CH_3)_2H:B(C_6F_5)_4$ or
$(C_6H_5)_3C:B(C_6F_5)_4$. Other borates of general formula

$(cation^+)_a$ $(borate^-)_b$ where a and b are positive numbers, may also be used.

Where such a cocatalyst or catalyst activator is used, it is preferably used in a mole ratio to the metallocene of from 0.1:1 to 10000:1, especially 1:1 to 50:1, particularly 1:2 to 30:1. More particularly, where an alumoxane cocatalyst is used, then for an unsupported catalyst the aluminium:metallocene metal (M) molar ratio is conveniently 2:1 to 10000:1, preferably 50:1 to 1000:1. Where the catalyst is supported the Al:M molar ratio is conveniently 2:1 to 10000:1 preferably 50:1 to 400:1. Where a borane cocatalyst (catalyst activator) is used, the B:M molar ratio is conveniently 2:1 to 1:2, preferably 9:10 to 10:9, especially 1:1. When a neutral triarylboron type cocatalyst is used the B:M molar ratio is typically 1:2 to 500:1, however some aluminium alkyl would normally also be used. When using ionic tetraaryl borate compounds, it is preferred to use carbonium rather than ammonium counterions or to use B:M molar ratio below 1:1.

Where the further material is loaded onto the procatalyst loaded support material, the support may be recovered and if desired dried before use in olefin polymerization.

The olefin polymerized in the method of the invention is preferably ethylene or an alpha-olefin or a mixture of ethylene and an α-olefin or a mixture of alpha olefins, for example C_{2-20} olefins, e.g. ethylene, propene, n-but-1-ene, n-hex-1-ene, 4-methyl-pent-1-ene, n-oct-1-ene- etc. The olefins polymerized in the method of the invention may include any compound which includes unsaturated polymerizable groups. Thus for example unsaturated compounds, such as C_{6-20} olefins (including cyclic and polycyclic olefins (e.g. norbornene)), and polyenes, especially C_{6-20} dienes, may be included in a comonomer mixture with lower olefins, e.g. C_{2-5} α-olefins. Diolefins (ie. dienes) are suitably used for

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introducing long chain branching into the resultant polymer. Examples of such dienes include α,ω linear dienes such as 1,5-hexadiene, 1,6-heptadiene, 1,8-nonadiene, 1,9-decadiene, etc.

5   In general, where the polymer being produced is a homopolymer it will preferably be polyethylene or polypropylene. Where the polymer being produced is a copolymer it will likewise preferably be an ethylene or propylene copolymer with ethylene or propylene making up

10   the major proportion (by number and more preferably by weight) of the monomer residues. Comonomers, such as C_{4-6} alkenes, will generally be incorporated to contribute to the mechanical strength of the polymer product.

Usually metallocene catalysts yield relatively

15   narrow molecular weight distribution polymers; however, if desired, the nature of the monomer/monomer mixture and the polymerization conditions may be changed during the polymerization process so as to produce a broad bimodal or multimodal molecular weight distribution

20   (MWD) in the final polymer product. In such a broad MWD product, the higher molecular weight component contributes to the strength of the end product while the lower molecular weight component contributes to the processability of the product, e.g. enabling the product

25   to be used in extrusion and blow moulding processes, for example for the preparation of tubes, pipes, containers, etc.

A multimodal MWD can be produced using a catalyst material with two or more different types of active

30   polymerization sites, e.g. with one such site provided by the metallocene on the support and further sites being provided by further catalysts, e.g. Ziegler catalysts, other metallocenes, etc. included in the catalyst material.

35   Polymerization in the method of the invention may be effected in one or more, e.g. 1, 2 or 3, polymerization reactors, using conventional

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polymerization techniques, e.g. gas phase, solution phase, slurry or bulk polymerization.

In general, a combination of slurry (or bulk) and at least one gas phase reactor is often preferred, particularly with the reactor order being slurry (or bulk) then one or more gas phase.

For slurry reactors, the reaction temperature will generally be in the range 60 to 110°C (e.g. 85-110°C), the reactor pressure will generally be in the range 5 to 80 bar (e.g. 50-65 bar), and the residence time will generally be in the range 0.3 to 5 hours (e.g. 0.5 to 2 hours). The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100°C. In such reactors, polymerization may if desired be effected under supercritical conditions.

For gas phase reactors, the reaction temperature used will generally be in the range 60 to 115°C (e.g. 70 to 110°C), the reactor pressure will generally be in the range 10 to 25 bar, and the residence time will generally be 1 to 8 hours. The gas used will commonly be a non-reactive gas such as nitrogen together with monomer (e.g. ethylene).

For solution phase reactors, the reaction temperature used will generally be in the range 130 to 270°C, the reactor pressure will generally be in the range 20 to 400 bar and the residence time will generally be in the range 0.1 to 1 hour. The solvent used will commonly be a hydrocarbon with a boiling point in the range 80-200°C.

Generally the quantity of catalyst used will depend upon the nature of the catalyst, the reactor types and conditions and the properties desired for the polymer product. Conventional catalyst quantities, such as described in the publications referred to herein, may be used.

All publications referred to herein are hereby incorporated by reference.

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EXPERIMENTAL

General Considerations

All operations were carried out in argon or nitrogen
atmosphere using standard Schlenk, vacuum and dry box
techniques. Solvents were dried with potassium
benzophenone ketyl and distilled under argon prior to
use. 1.5.7-triaza[4.4.0]bicyclo-dec-5-ene (TAB-H)
(Fluka) and dipyridylketone (DPM-H) (Fluka) were used as
purchased. Benzyl potassium was prepared according to
Schlosser, M. and Hartmann, J. Angew. Chem 1973, 85,
544-545. $CrCl_3(THF)_3$ and $TiCl_3(THF)_3$ were prepared
according to W.A. Herrmann and G. Brauer, Synthetic
Methods of Organometallic and Inorganic Chemistry, Vol.
1: Literature, Laboratory Techniques and Common Starting
Materials, Thieme 1996. 1H- and 13C-NMR spectra were
recorded using JEOL JNM-EX 270 MHz FT NMR spectrometer
with tetramethylsilane (TMS) as an internal reference.
13C-CPMAS NMR and the mass spectra were recorded at
Fortum Oil and Gas Oy, Analytical Research department.
The CPMAS-NMR spectra were recorded using Chemagnetics
Infinity 270 MHz equipment and the direct inlet MS
spectra were produced by VG TRIO 2 quadrupole mass
spectrometer in electron impact ionisation mode (EIMS)
(70eV). The GC-MS analyses were performed using Hewlett
Packard 6890/5973 Mass Selective Detector in electron
impact ionisation mode (70eV) equipped with a silica
capillary column (30 m x 0.25 mm i.d.). The FTIR spectra
were recorded at Borealis Analytical Research department
using Perkin-Elmer Spectrum 2000 spectrometer with inert
diamond ATR accessory and 4 cm-1 resolution.
Thermogravic measurements (TG) were recorded using GWB
METTLER TG50 Termobalance and the Differential Scanning
Calorimetry (DSC) and melting point analyses using GWB
METTLER DSC-30 under inert conditions at Borealis

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Analytical Research department. The polymerization tests
were carried out using MAO, 30 % solution in toluene
purhased from Albermarle. Test polymerizations were
carried out in pentane at 60°C and at 80°C with hydrogen
5   present using an Al/M ratio of 1000 unless otherwise
stated. A Büchi 2 L stirred reactor with mantle heating
was used for the polymerization tests.

10   **Example 1**
Synthesis of (1.5.7-triaz[4.4.0]bicyclo-dec-5-enyl)
potassium, $C_7H_{12}KN_3$
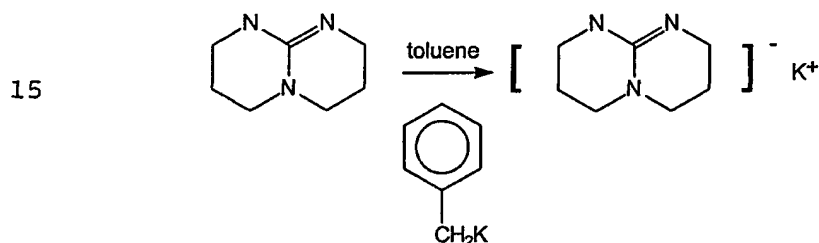
20   Red solid benzyl potassium (9.6g, 73.3 mmol) was added
into the solution of 1.5.7-triaza[4.4.0]bicyclo-dec-5-
ene (10.2g, 73.3 mmol) in 350 ml of dry toluene at
-40°C. The temperature was allowed to warm to room
temperature and the mixture stirred for 16 hours. The
25   colour changed via red to a white slurry. The solvents
were removed in a vacuum, the product washed with 3 x 60
ml of ether and dried in a vacuum to obtain 10.1g (78%)
of white powder. ^{1}H-NMR in THF-d_8; δ: 3.17 (t, 4H); 2.98
(t, 4H); 1.69 (t, 4H). The potassium salt product could
30   not be analysed with MS. Elemental analysis calc.: C
47.4%, H 6.8%, N 23.7%, K 22.1%. Elemental analysis
found: C 46.0%, H 6.4%, N 23.1%.

Example 2
35   **Synthesis of triazabicyclodec-ene-yl-1-**
dimethylsilylchloride $C_9H_{18}ClN_3Si$.
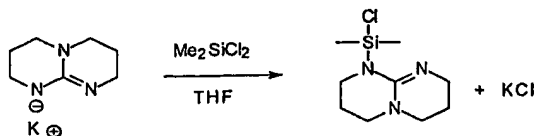
1.5.7-triaza[4.4.0]bicyclo-dec-5-enyl potassium 13.0 g
(73.1 mmol) dissolved in 200 mL of THF was added into a
solution of 55 mL (438.6 mmol) of Me_2SiCl_2 in 50 mL THF
over 3 hours at ambient temperature. Colour changed from
yellow to dark yellow. The solution was stirred for 2
hours at ambient temperature after which the mixture
containing a gelish precipitate of KCl was filtrated and
washed with 2 x 30 mL of THF. Solvent was removed under
vacuum to obtain an off yellow solid which was extracted
with 3 x 30 mL of pentane and and filtrated. The product
was purified by recrystallization and filtration from
cold (-30°C) pentane yielding colorless, needle-like
crystals. Yield 12.9 g (76.4%). ^{1}H-NMR $CDCl_3$ δ: 3.16 (t,
4H), 3.11 (t, 4H), 1.88 (t, 4H), 0.46 (s, 6H). ^{13}C-NMR
$CDCl_3$ δ: 154.9, 45.3, 38.6, 23.3, 7.9. EIMS analysis
showed the decomposition pattern of the parent ion of
the title compound $C_9H_{18}ClN_3Si$ M^+=231.80 g mol^{-1}.
Elemental analysis calc. C 46.63%, H 7.83%, N 18.13%, Cl
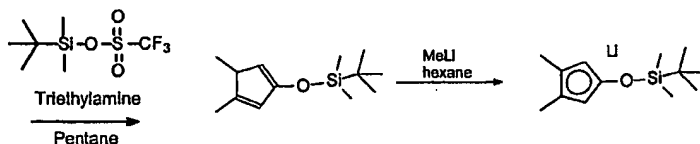15.29%, Si 12.12%; Found. C 46.52%, H 7.80%, N 18.24%,
Cl 15.15%, Si 12.05%.

Example 3
t-Butyldimethylsiloxy-3,4-dimethylcyclopentadienyl
lithium
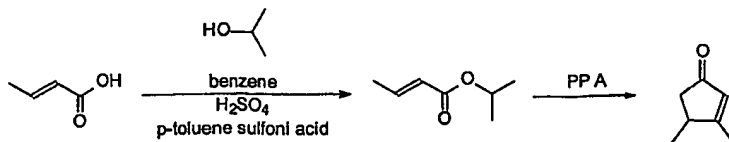
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40.0 g (465 mmol) of crotonic acid (Fluka 28010), 25.1 g
(418 mmol) of isopropanol (Merck 1.09634.2500), 200 mL
of benzene, 4.2 g of conc. H_2SO_4 and 2.1 g of *para*-
toluene sulfonic acid was charged to a 500 mL flask
5   equipped with a magnetic stirrer bar and Dean-Stark
water separator. The mixture was refluxed until water
formation ceased. 200 mL of ether was added to the
mixture, and then washed with several portions of $NaHCO_3$
(aq., sat.) until the the acid was neutralized. Organic
10   phase was separated, dried with $MgSO_4$ and filtered.
Solvent was removed under reduced pressure and the
remainder distilled at 95°C to give 30.5 g of
isopropylcrotonate. Yield 57%. ^{1}H-NMR ($CDCl_3$): 6.95 (dq,
1H), 5.82 (d, 1H), 5.05 (sept, 1H), 1.88 (d, 3H), 1.25
15   (d, 6H).

811 g of polyphosphoric acid (Fluka 81340) was loaded to
a round bottom flask equipped with a reflux condenser
and a magnetic stirrer bar and heated to 100°C. 104 g
20   (810 mmol) of isopropylcrotonate was added to the flask
and the mixture was stirred for 2 hours at 100°C. The
resulted mixture was poured to »1,5 kg of crushed ice. At
room temperature the mixture was saturated with NH_4Cl and
extracted with 4x100 mL of ether. The combined ether
25   fractions were dried over $MgSO_4$ and filtered. Solvent was
removed under reduced pressure and the remainder
distilled (0.2 mbar, 33°C, bath 90°C) to give 47.99 g of
3,4-dimethylcyclopentenone. Yield 54%. ^{1}H-NMR ($CDCl_3$):
5.86 (s, 1H), 2.80 (m, 1H), 2.64 (dd, 1H), 2.07 (s, 3H),
30   2.00 (dd, 1H), 1.18 (d, 3H).

12.23 g (111.0 mmol) of 3,4-dimethylcyclopentenone,
11.31 g (111.8 mmol) of triethylamine dried with
molecular sieves and 300 mL of dry pentane were mixed at
35   room temperature. During 13 minutes 29.44 g (111.4 mmol)
of t-butyldimethylsilyltrifluoromethylsulfonate (Fluka
97742) was added to the mixture. After stirring for 2.5

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hour the supernatant pentane fraction was separated, solvent removed under reduced pressure and the remainder distilled (0.03 mbar, 34-40°C, bath 100°C) resulting in 19.74 g of isomer isomer mixture of t-
5   butyldimethylsiloxy-3,4-dimethylcyclopentadienes. Yield 79%. ^{1}H-NMR spectrum was complicated due to presence of at least 3 isomers. The product was characterised by GC/MS technique, which showed presence of three components (GC) each showing M+ peak at 224 (MS).
10

10 g (44.6 mmol) of isomer mixture of t-butyldimethyl-siloxy-3,4-dimethylcyclopentadienes was mixed with 200 mL of pentane at room temperature. At -20°C 28.4 mL (44.6 mmol) of 1.57 M t-butyllithium solution in hexanes
15   (Acros 18128-0900) was added. Temperature was increased to 20°C during 15 hours while stirring. The resulted solid product was separated by filtration and washed with 2 x 100 mL of pentane. Remaining solvent was removed under reduced pressure. 7.07 g of t-butyl-
20   dimethylsiloxy-3,4-dimethylcyclopentadienyl lithium was isolated. Yield 69%. ^{1}H-NMR (THF-d$_8$): 4.88 (s, 2H), 1.95 (s, 6H), 0.95 (s, 9H), 0.08 (s, 6H).

Example 4
25   **Synthesis of *Tri*-isopropylsiloxycyclopentadienyl lithium**

30
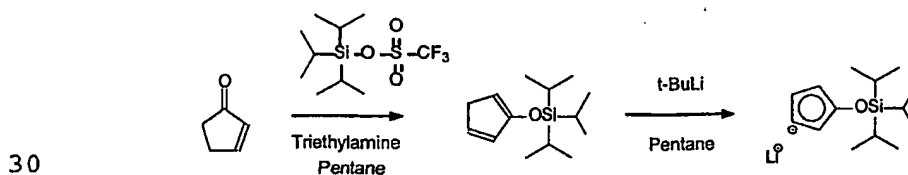
Triisopropylsiloxycyclopentadiene was prepared analogously to example 3 using triisopropylsilyl-trifluoromethylsulfonate (Fluka 91746) and cyclopent-2-
35   enone (Fluka 29827) as starting materials. It was not isolated but lithiated immediately to avoid spontaneous Diels-Alder dimerisation of the product. Lithiation was
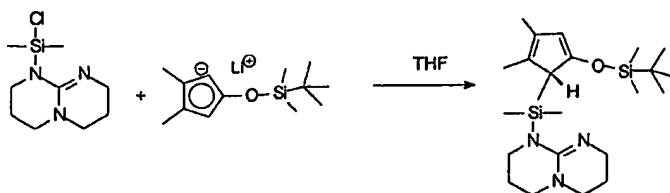
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performed analogously to example 3 and afforded triisopropylsiloxycyclopentadienyl lithium in 81% yield. ^{1}H-NMR (THF-d_8): 5.22 (m, 2H), 5.17 (m, 2H), 1.11 (m, 3H), 1.04 (d, 18H).

Example 5
Synthesis of triazabicyclodec-ene-yl-1-dimethylsilyl-dimethyl-tertbutylsiloxy dimethylcyclopentadiene (mixture of isomers) $C_{22}H_{41}N_3OSi_2$

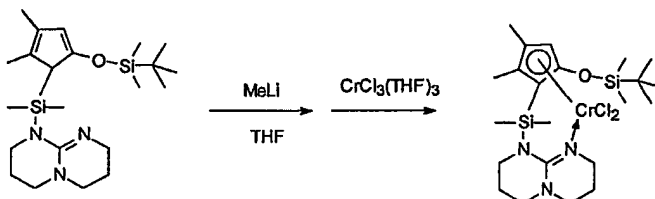

1.2 g (5.21 mmol) of t-butyldimethylsiloxy-3,4-dimethylcyclopentadienyl lithium dissolved in 100 mL of THF was added over 1 h into a solution of 1.2 g (5.21 mmol) of triazabicyclodec-ene-yl-1-dimethylsilylchloride in 50 mL of THF at -70°C to give an orange transparent solution. The solution was refluxed for 16 hours after which the solvent was removed under vacuum. The product was extracted into pentane, filtrated and cooled to -30°C for 16 hours. Trace insolubilities were filtrated off at -30°C and the solvent removed under vacuum to give 98% pure, brown oily mixture of double bond and stereoisomers. Yield 1.6 g (73.3%). The EIMS analysis showed the decomposition pattern of the parent ion of the title compound $C_{22}H_{41}N_3OSi_2$ M^+=419.76 g mol^{-1}, fragmentation peaks at 404, 270, 224 and 196. ^{1}H-NMR of the major isomer in THF-d_8 δ: 5.02 (s, 1H) 3.41 (s, 1H) 3.18 (m, 4H) 3.06 (m, 4H) 2.02 (s, 3H) 1.95 (s, 3H) 1.78 (m, 4H) 0.97 (s, 9H) 0.24 (s, 3H), 0.22 (s, 3H), 0.19 (s, 3H), 0.10 (s, 3H). ^{13}C-NMR THF-d_8 δ: 160.9, 151.6, 131.7, 124.6, 110.6, 95.5, 53.0, 48.9, 43.3, 27.0, 26.4, 24.7, 13.0, 0.9, -4.1, -4.6.

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Example 6
Synthesis of triazabicyclodec-ene-yl-1-dimethylsilyl-
dimethyl-tertbutylsiloxy dimethylcyclopentadienyl
chromium dichloride $C_{22}H_{40}Cl_2CrN_3OSi_2$

5

10

1.8 mL of MeLi (1.6 M solution in diethyl ether, 3.34
mmol) was added into a solution of
1.6 g (3.34 mmol) of triazabicyclodec-ene-yl-1-
dimethylsilyl-dimethyl-tertbutylsiloxy
15   dimethylcyclopentadiene in 50 mL THF at +50°C over 5
minutes and stirred at ambient temperature for 16 hours.
$CrCl_3(THF)_3$ (3.34 mmol) dissolved in THF was added over
40 minutes at -50°C to give a dark blue solution which
was stirred at ambient temperature for 16 hours.
20   Solvents were removed under vacuum and the product
extracted in toluene, filtered and evaporated. The raw
product was purified by washing with cold pentane. Yield
1.0 g (52.2%) of dark blue microcrystalline solid. The
compound was paramagnetic, NMR identification was not
25   possible. The EIMS analysis showed the decomposition
pattern of the parent ion of the title compound
$C_{22}H_{40}Cl_2CrN_3OSi_2$ $M^+=541.65$ g mol^{-1}, fragmentation peaks at
504, 468, 418, 287, 224, 196 and 138. Melting point:
145°C (broad peak in DSC). TG analysis (from 30°C to
30   891°C, 10°C/min) showed 57.7% loss of weight in a one
phase process at 286°C averaged delta temperature.
Crystals suitable for X-ray analysis were not obtained
because of the presence of the two stereoisomers (rac
and meso type) which resulted in the precipitation of
35   microcrystalline solid. Elemental analysis calc.
C 48.78%, H 7.44%, N 7.76%, Cl 13.09%, Si 10.37%, Cr
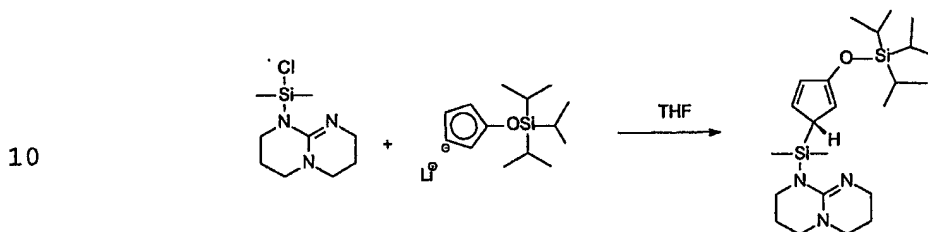9.60%; Found C 49.02%, H 7.56%, N 7.94%, Cl 12.91%, Si

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10.11%, Cr 9.44%.

Example 7
Synthesis of triazabicyclodec-ene-yl-1-dimethylsilyl-
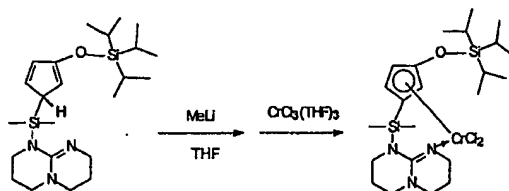*tri*-isopropylsiloxy cyclopentadiene (mixture of isomers)
$C_{23}H_{43}N_3OSi_2$

3.2 g (12.3 mmol, 92.6%) of *tri*-isopropylsiloxy-
cyclopentadienyl lithium dissolved in 70 mL of THF was
added over 40 minutes into a solution of 2.8 g (12.3
mmol) of triazabicyclodec-ene-yl-1-dimethylsilylchloride
in 70 mL of THF at -70°C to give a red mixture. The
mixture was refluxed for 16 hours after which the
solvent was removed under vacuum. The product was
extracted into pentane, filtrated and the filtrate
cooled to -30°C for 16 hours after which the insolubles
were filtered off at -30°C. The filtrate was then cooled
to -70°C for 6 h and the trace insolubles filtrated off
at -70°C. The pentane was then removed under vacuum to
give a dark brown, viscous oily mixture of double bond
and regioisomers. Yield 3.1 g (57.6%). The EIMS analysis
showed the decomposition pattern of the parent ion of
the title compound $C_{23}H_{43}N_3OSi_2$ $M^+=433.78$ g mol^{-1},
fragmentation peaks at 418, 390, 238 and 196. ^{1}H-NMR
major isomer in THF-d$_8$ δ: 6.39 (m, 1H) 6.21 (m, 1H) 5.62
(m, 1H) 3.19 (m, 4H) 3.08 (m, 4H) 2.92 (m, 1H) 1.80 (m,
4H) 1.20 (m, 3H) 1.18 (s, 18H) 0.25 (s, 6H). ^{13}C-NMR
major isomer (1,3-substituted regioisomer) in THF-d$_8$ δ:
149.0, 131.8, 130.8, 130.0, 105.0, 102.0, 47.0, 41.2,
22.7, 16.2, 11.2, 0.4. The compound decomposed during
the elemental analysis sample preparation.

Example 8

Synthesis of triazabicyclodec-ene-yl-1-dimethylsilyl-*tri*-isopropylsiloxy cyclopentadienyl chromium dichloride (mixture of isomers) $C_{23}H_{42}N_3Cl_2CrOSi_2$


3.7 mL of MeLi (1.9 M solution in diethyl ether, 7.04 mmol) was added into a solution of 3.1 g (7.04 mmol) of triazabicyclodec-ene-yl-1-dimethylsilyl-*tri*-isopropylsiloxy-cyclopentadiene in 70 mL THF at +50°C over 5 minutes and stirred at ambient temperature for 16 hours. $CrCl_3(THF)_3$ (7.04 mmol) dissolved in 50 mL THF was added over 30 minutes at -30°C to give a dark blue-green solution which was stirred at ambient temperature for 16 hours. Solvents were removed under vacuum and the product extracted in toluene, filtered and evaporated. The raw product was purified by washing with cold pentane. Yield 1.9 g (48.6%) of blue-green microcrystalline solid. The compound was paramagnetic, NMR identification was not possible. The EIMS analysis showed the decomposition pattern of the parent ion of the title compound $C_{23}H_{42}Cl_2CrN_3OSi_2$ $M^+=555.68$ g mol^{-1}, fragmentation peaks at 499, 477, 238, 192 and 178. Melting point: 170.9 °C (broad peak in DSC). TG analysis (from 30°C to 891°C, 10 °C/min) showed 55.2% loss of weight in a two phase process at 242 °C averaged delta temperature. Mp 170.9°C. Crystals suitable for X-ray analysis were not obtained because of the presence of the two stereoisomers (rac and meso type) which resulted in the precipitation of microcrystalline solid. Elemental analysis calc. C 49.71%, H 7.62%, N 7.56%, Cl 12.76%, Cr 9.36%, O 2.88%,

Si 10.11%; Found C 49.50%, H 7.65%, N 7.31%, Cl 12.93%, Si 9.98%, Cr 9.48%.

Example 9

Synthesis of triazabicyclodec-ene-yl-1-dimethylsilyl-fluorene $C_{22}H_{27}N_3Si$
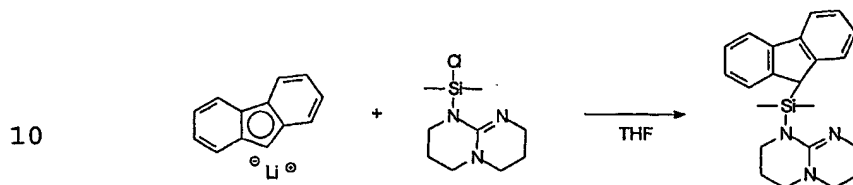
Fluorenyllithium (prepared from fluorene via treatment of butyllithium) 0.7 g (4.08 mmol) dissolved in 50 mL of THF was added over 30 minutes into a solution of 0.9 g (4.08 mmol) of triazabicyclodec-ene-yl-1-dimethyl-silylchloride in 50 mL of THF at -70°C. The yellowish solution was stirred at ambient temperature for 16 hours after which the solvent was removed under vacuum. The product was extracted into pentane, filtrated and cooled to -30°C for 16 hours. The product precipitated as yellowish transparent crystals which were filtrated and dried in a vacuum. Yield 1.1 g (73.8%). The EIMS analysis showed the decomposition pattern of the parent ion of the title compound $C_{22}H_{41}N_3OSi_2$ $M^+=361.56$ g mol^{-1}, fragmentation peaks at 346, 196, 165 and 138. ^{1}H-NMR in CDCl$_3$ δ: 7.90 (d, 2H), 7.58 (d, 2H), 7.38 (dd 2H) 7.30 (dd, 2H), 4.95 (s, 1H) 3.22 (t, 4H) 3.19 (t, 4H) 1.91 (q, 4H) -0.1 (s, 6H). ^{13}C-NMR in CDCl$_3$ δ: 161.3, 146.3, 140.7, 125.7, 124.7, 124.3, 119.5, 48.3, 43.2, 42.7, 23.8, -2.5.
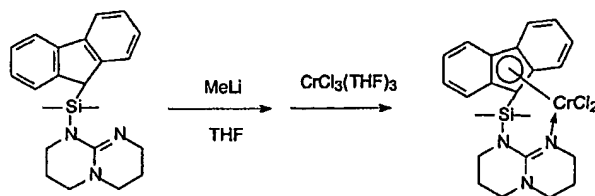
Example 10

Synthesis of triazabicyclodec-ene-yl-1-dimethylsilyl-fluorenyl chromium dichloride $C_{22}H_{26}Cl_2CrN_3Si$ (descriptive example)

5

10

1.7 mL of methyl lithium (2.94 mmol, 1.76 M solution in diethyl ether) was added at -30°C into a solution of triazabicyclodec-ene-yl-1-dimethylsilyl-fluorene 1.1 g (2.94 mmol) in 50 mL of THF. The solution became bright
15 neon yellow and yellowish precipitate formed. The mixture was stirred at ambient temperature for 16 hours. Then $CrCl_3(THF)_3$ (2.94 mmol) dissolved in 50 mL THF was added into the solution at -30°C and the mixture stirred at ambient temparature for 16 hours. Solvents were
20 removed under a vacuum and the product extracted in toluene, filtered and evaporated. The paramagnetic product was purified by washing with cold pentane and evaporated.

25 **Example 11**

Synthesis of triazabicyclodec-ene-yl-1-diphenylsilylchloride $C_{19}H_{22}ClN_3Si$

30
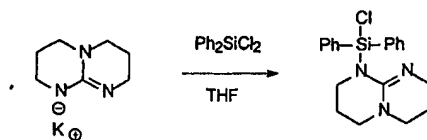
1.5.7-Triaza[4.4.0]bicyclo-dec-5-enyl potassium 3.0 g
35 (16.9 mmol) dissolved in 50 mL of THF was added into a solution of 21 mL (101.5 mmol) of Ph_2SiCl_2 in 50 mL THF over 3 hours at ambient temperature. Colour changed from

- 33 -

whitish to light yellow. The solution was stirred for 2
hours at ambient temperature after which the mixture
containing a gelish precipitate of KCl was filtrated and
washed with 2x30 mL of THF. Solvents were removed under
vacuum to obtain a slightly viscous liquid. Then 50 mL
of pentane was added to the filtrate and the
precipitated product separated by filtration and washed
with 2x30 mL of more pentane. Yield 5.2 g (87.3%) of
white solid. ^{1}H-NMR CDCl$_3$ δ: 7.52 (dd, 4H), 7.34 (d, 2H),
7.32 (d, 4H), 3.25 (m, 4H), 3.15 (t, 4H), 1.96 (q, 4H).
^{13}C-NMR CDCl$_3$ δ: 155.1, 141.0, 134.0, 128.3, 127.2, 46.6,
38.8, 23.2. The EIMS analysis showed the decomposition
pattern of the parent ion of the title compound
C$_{19}$H$_{22}$ClN$_3$Si M$^+$=355.94 g mol^{-1}, frgamentation peaks at 320,
278 and 138. Elemental analysis calc. C 64.11%, H
6.23%, N 11.81%, Cl 9.96%, Si 7.89%; Found C 63.89%, H
6.20%, N 11.97%, Cl 9.90%, Si 7.74%.

Example 12
**Synthesis of triazabicyclodec-ene-yl-1-diphenylsilyl-
tetramethylcyclopentadiene C$_{28}$H$_{35}$N$_3$Si**
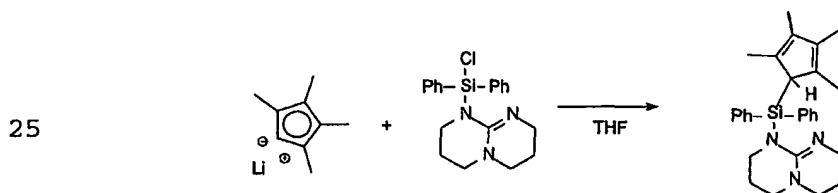
Tetramethylcyclopentadienyl lithium 1.04 g (8.15 mmol)
(prepared from tetramethylcyclopentadiene via treatment
of *n*-butyllithium) dissolved in 50 mL THF was added into
a solution of triazabicyclodec-ene-yl-1-diphenyl-
silylchloride in 50 mL of THF over 20 minutes at -30°C.
The mixture was stirred at ambient temperature for 16
hours, after which the solvents were removed under
vacuum, the product extracted in pentane, filtered and
evaporated. Yield 2.2g (61.1%) of white solid. The
EIMS analysis shows the decomposition pattern of the

- 34 -

parent of the title compound $C_{28}H_{35}N_3Si$ M^+ 441.69 $gmol^{-1}$.
^{1}H-NMR THF-d_8 δ: 7.54 (d, 4H), 7.22 (m, 4H), 7.20 (d,
4H), 4.21 (s, 1H), 3.17 (t, 4H), 3.03 (t, 4H), 1.83 (s,
6H), 1.75 (m, 4H), 1.42 (s, 6H). ^{13}C-NMR THF-d_8 δ:
151.9, 136.8, 136.7, 136.6, 133.3, 128.9, 126.9, 54.8,
48.6, 43.4, 24.7, 14.5, 11.6. Elemental analysis calc.
C 76.14%, H 7.99%, N 9.51%, Si 6.36%; Found C 76.04%, H
8.13%, N 9.54%, Si 6.38%.

Example 13

**Synthesis of triazabicyclodec-ene-yl-1-diphenylsilyl-
tetramethylcyclopentadienyl chromium dichloride
$C_{28}H_{34}Cl_2CrN_3Si$**
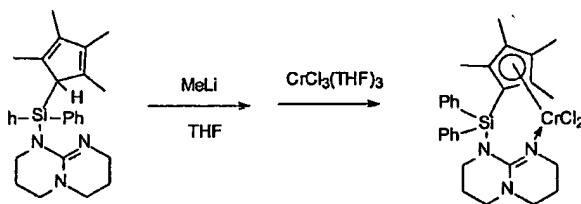
4.6 mL of methyl lithium (8.15 mmol, 1.76 M solution in
diethyl ether) was added into a solution of
triazabicyclodec-ene-yl-1-diphenylsilyl-
tetramethylcyclopentadiene in 50 mL of THF at -30°C. The
solution was stirred at ambient temperature for 16
hours. A whitish precipitate formed. Then $CrCl_3(THF)_3$
dissolved in 50 mL of THF (8.15 mmol) was added over 30
minutes at -30°C, and the mixture stirred 16 hours at
ambient temperature. The solvent was removed under
vacuum and the product extracted in toluene, filtered
and evaporated. EIMS $M^\oplus$ = 563.59 $gmol^{-1}$. Elemental
analysis calc. C 59.67%, H 6.08%, N 7.46%, Cl 12.58%, Si
4.98%, Cr 9.23%; Found C 59.42%, H 6.23%, N 7.52%, Cl
12.82%, Si 5.05%, Cr 9.35%.

- 35 -

Example 14
Synthesis of trimethylsiloxycyclopentadiene

5
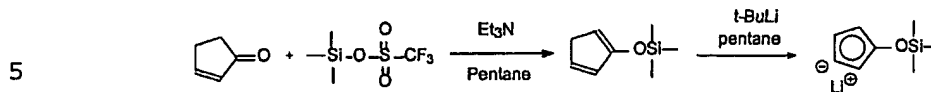
Scheme 1.

9.1 g (111.0 mmol) of cyclopent-2-en-1-one (Fluka
10   29827), 11.31 g (111.8 mmol) of triethylamine dried with
molecular sieves and 300 mL of dry pentane are mixed at
room temperature. Over 13 minutes 24.75g (111.4 mmol) of
trimethylsilyl-trifluoromethylsulfonate (Fluka 91741) is
added to the mixture. After strirring for 2.5 hour the
15   supernatant pentane fraction is separated, solvent
removed under reduced pressure and the remainder
distilled under reduced pressure resulting in an isomer
mixture of trimethylsiloxycyclopentadienes. The product
is characterised by ^{1}H-NMR and GC/MS$^+$.
20   Trimethylsiloxycyclopentadienyl lithium is prepared as
described in the last section of example 3 by using t-
BuLi.
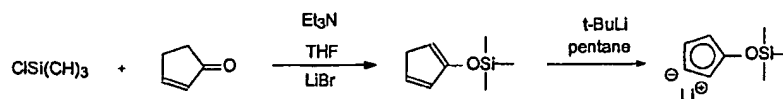
Scheme 2.
Trimethylsiloxycyclopentadiene can also be synthesised
25   according to the description in Acta. Chem.
Scandinavica, 43, 1989, 188-92 (Scheme 2). 1.74 g of
LiBr (20 mmol, dried under vacuum at 400°C) is dissolved
in 5.55 g of THF (77 mmol). At -15°C, 1.54 g of
chlorotrimethylsilane (15 mmol), 1.23 g of cyclopent-2-
30   en-1-one (15 mmol) and 1.51 g of triethylamine (15 mmol,
dry) are added to the solution. After 1 hour at -15°C
and 24 hours at +40°C the crude product is isolated by
low temperature aquous NaCl/NaHCO$_3$ and pentane

extractions. The crude trimethylsiloxycyclopentadienes
are purified by distillation under reduced pressure.
Trimethylsiloxycyclopentadienyl lithium is prepared as
described in the last section of example 3 by using t-
5   BuLi.

Example 15
Synthesis of triazabicyclodec-ene-yl-1-diphenylsilyl-
trimethylsiloxycyclopentadiene $C_{27}H_{35}N_3OSi_2$

10

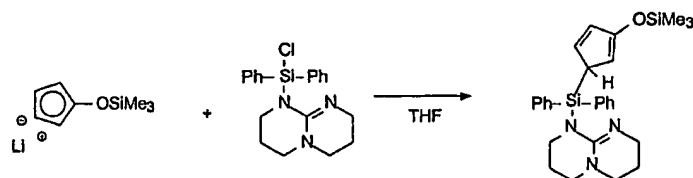15   Trimethylsiloxycyclopentadienyl lithium (8.15 mmol)
(prepared from trimethylsiloxycyclopentadiene via
treatment of t-butyllithium) dissolved in 50 mL THF is
added into a solution of triazabicyclodec-ene-yl-1-
diphenylsilylchloride in 50 mL of THF over 20 minutes at
20   -30°C. The mixture is stirred at ambient temperature for
16 hours, after which the solvents are removed under
vacuum, the product extracted in pentane, filtered and
the major kinetically formed isomer with 1,3-
substitution pattern of the siloxy and the bridge
25   subtituents on the Cp ring is obtained via
recrystallization from cold pentane.

Example 16
Synthesis of triazabicyclodec-ene-yl-1-diphenylsilyl-
30   **trimethylsiloxycyclopentadienyl chromium dichloride**
**$C_{27}H_{34}Cl_2CrN_3OSi_2$**

35
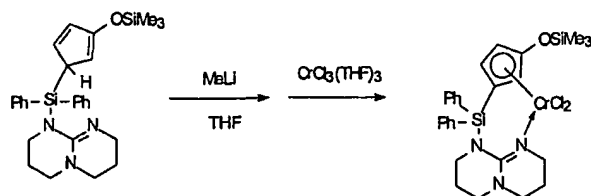
- 37 -

Methyl lithium (8.15 mmol, 1.76 M solution in diethyl
ether) is added into a solution of triazabicyclodec-ene-
yl-1-diphenylsilyl-tetramethylcyclopentadiene in 50 mL
of THF at -30°C. The solution is stirred at ambient
temperature for 16 hours. A whitish precipitate forms.
Then $CrCl_3(THF)_3$ dissolved in 50 mL of THF (8.15 mmol) is
added over 30 minutes at -30°C, and the mixture stirred
16 hours at ambient temperature. The solvent is removed
under vacuum and the product extracted in toluene,
filtered and evaporated to give a blue solid product.

Example 17
Synthesis of dipyridin-2-ylmethane $C_{11}H_{10}N_2$
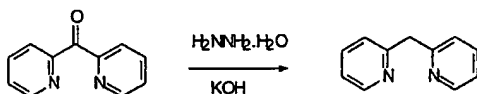
Solid KOH (9.4 g, 167.7 mmol) was dissolved in 15 mL of
distilled water and poured into an autoclave reactor
(Parr pressure reactor) under nitrogen atmosphere. Di(2-
pyridyl) ketone (15.0 g, 81.4 mmol) was weighed and
introduced into the reactor. Hydrazine monohydrate
(6.1 mL, 185.7 mmol) was poured into the reaction
mixture and the reactor closed. The reactor was mounted
on a Parr heater unit and the reaction mixture stirred
for 18h at 150°C at 28 bar. After 1 hour the temperature
was 150°C and the pressure 5 bar. After 18h heating and
stirring the temperature was 151°C and the pressure
inside the reactor 28 bar. After the reaction was
complete, the cooled reactor was opened at air
atmosphere and the yellowish liquid obtained neutralized
with 1M HCl (aq.) and extracted with 3x50 mL chloroform.
Organic phase was washed with 3x30 mL of brine and dried
over $MgSO_4$. Solvents were removed in a vacuum and the
crude product distilled in a vacuum to obtain a yellow
liquid with b.p. 80-85°C/0.06 mbar. Yield: 9.8 g (72%).

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^{1}H-NMR in CDCl$_3$; δ: 8.48 (m, 2H); 7.51 (m, 2H); 7.19 (t, 2H); 7.04 (m, 2H); 4.29 (s, 2H). EIMS analysis showed parent ion of the title compound C$_{11}$H$_{10}$N$_2$ corresponding to molecular weight M$^+$=170.21 g mol^{-1}.

Example 18
Synthesis of dipyridin-methan-2-yl-potassium C$_{11}$H$_9$KN$_2$
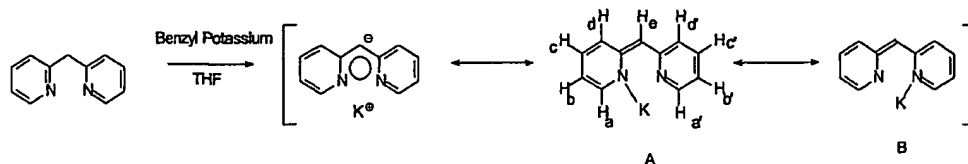
Benzyl potassium 4.0 g (30.5 mmol) was added into a solution of dipyridin-2-ylmethane 5.2 g (30.5 mmol) in 100 mL THF at -70°C over 10 minutes. The mixture was stirred at ambient temperature for 16 hours after which the bright yellow mixture was filtrated and washed with THF. Solvents were evaporated and the product washed with pentane and evaporated to yield a bright yellow solid which on the basis of the ^{1}H-NMR spectrum in DMSO-d$_6$ was [DPM$^-$K$^+$][THF]$_{0.5}$. Yield 5.44 g (73.0%) based the THF complex (M$_W$=244.35 g mol^{-1}). The product decomposed during EIMS analysis. Elemental analysis calculated for [DPM$^-$K$^+$][THF]$_{0.5}$: C 64.6%, H 4.8%, N 12.0%, K 21.9%. Found: C 63.9%, H 5.36%, N 11.46%, K 16.0%. NMR spectra were recorded at +22.7°C, +50°C and at +70°C in DMSO-d$_6$. The complex shows fluxional behaviour in NMR with increasing temperature which is caused by the transition between the two resonance structures A and B. The peaks coalescence at +70°C. The singlet bridgehead proton is exchanged slowly with the methyl deuterium of DMSO-d$_6$ which is seen as an appearing triplet in ^{13}C-NMR . ^{1}H-NMR in DMSO-d$_6$ at +70°C δ: 8.20 and 6.25 (broad coalesence peaks, 2H, from H$_a$↔H$_{a'}$), 7.65 (d, 2H, from H$_d$↔H$_{d'}$), 6.78 (broad, 2H, from H$_b$↔H$_{b'}$), 5.76 (broad, 2 H, from H$_c$↔H$_{c'}$), 4.62 (s, 1H, exchangeable proton H$_e$). ^{13}C-NMR in DMSO-d$_6$ at δ: 160.2, 147.9, 147.8, 132.3, 131.2, 116.9, 114,3,

- 39 -

105.3, 103.3, triplet 87.2 from exchanged CH$_e$↔DMSO-d$_6$.^{13}C-
CPMAS δ: 163, 150, 138, 119, 109, 82.

Example 19

**Synthesis of triazabicyclodec-ene-yl-1-dimethylsilyl-
dipyridin-methane C$_{20}$H$_{27}$N$_5$Si**
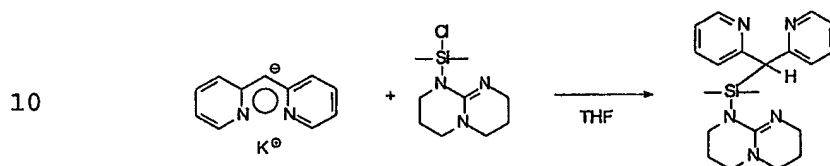
Dipyridin-methan-2-yl-potassium 2.62 g (12.6 mmol)
dissolved in 100 mL THF of was added into a solution of
triazabicyclodec-ene-yl-1-dimethylsilylchloride 2.90 g
(12.6 mmol) in 100 mL of THF over 40 minutes at -70°C.
The mixture was stirred at ambient temperature for 16
hours. Solvent was evaporated under vacuum, the product
extracted in toluene, filtrated and washed with more
toluene. Solvent was removed under vacuum and the
product grinded in glove box. The product was purified
by washing with cold pentane. Pentane solubles were
filtered off and the product evaporated under vacuum.
Yield 3.7 g (80.0%) of yellow solid. EIMS analysis
showed the decomposition pattern of parent ion of the
title compound C$_{20}$H$_{27}$N$_5$Si corresponding to molecular
weight M$^+$= 365.55 g mol^{-1}, fragmentation peaks at 335,
258, 196, 169, 138. ^{1}H-NMR in THF-d$_8$ δ: 8.45 (d, 2H),
7.45 (dd, 2H), 7.44 (d, 2H) 6.99 (t, 2H). 4.92 (s, 1H),
3.06 (t, 4H), 2.86 (t, 4H), 1.61 (q, 4H), 0.16 (s, 6H).
Elemental analysis calculated: C 65.7%, H 7.44%, N
19.2%. found: C 63.8%, H 6.8%, N 16.6%.

Example 20
Synthesis of triazabicyclodec-ene-yl-1-dimethylsilyl
dipyridylmethan-yl chromium dichloride C$_{20}$H$_{28}$Cl$_2$CrN$_5$Si

5
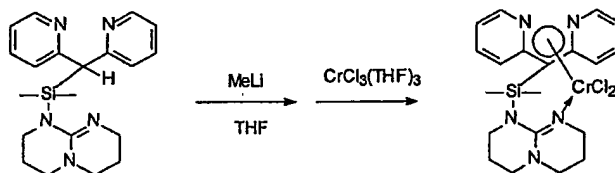
10   1.9 mL methyl lithium (3.7 mmol, 1.94 M solution in
      diethyl ether) was added into a solution of
      triazabicyclodec-ene-yl-1-dimethylsilyl dipyridylmethane
      1.33 g (3.6 mmol) dissolved in 100 mL THF at -30°C over
      5 minutes. The mixture was stirred at ambient
15   temperature for 2 hours. CrCl$_3$(THF)$_3$ (3.6 mmol) was added
      at -30°C over 30 minutes and the solution stirred at
      ambient temperature over 16 hours. Solvents were removed
      under vacuum, the product extracted in toluene, filtered
      and evaporated. The product was purified by washing with
20   cold dichloromethane and pentane. Yield 0.2 g (25.5%) of
      dark brown tar. The product decomposed during EIMS
      analysis. The product was paramagnetic, NMR
      identification could not be obtained.

25   **Example 21**
      **Synthesis of triazabicyclodec-ene-yl-1-dimethylsilyl
      dipyridylmethan-yl chromium dichloride C$_{20}$H$_{28}$Cl$_2$TiN$_5$Si**
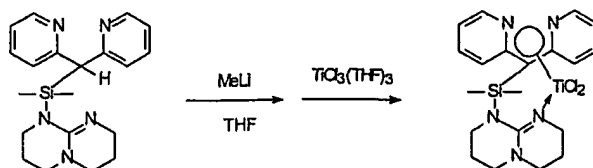
30

35   0.8 mL methyl lithium (1.64 mmol, 1.94 M solution in
      diethyl ether) was added into a solution of
      triazabicyclodec-ene-yl-1-dimethylsilyl dipyridylmethane

0.60 g (1.64 mmol) dissolved in 70 mL THF at -30°C over

5 minutes. The mixture was stirred at ambient

temperature for 16 hours. $TiCl_3(THF)_3$ (1.64 mmol) was

added at -70°C over 20 minutes and the solution stirred

5   at ambient temperature over 3 hours. Solvents were

removed under vacuum, the product extracted in toluene,

filtered and evaporated. The product was purified by

washing with cold dichloromethane and pentane. Yield

0.5g (64.9%) of dark brown tar. The product decomposed

10   during EIMS analysis. The product was paramagnetic, NMR

identification could not be obtained.

Example 22.

15   **Dimethylmethylene cyclopentadienyl triazabicyclodec-ene-**
yl-1 potassium $C_{15}H_{22}KN_3$

20
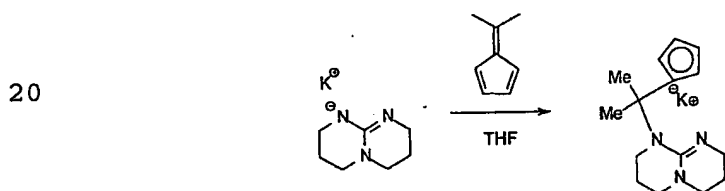
25   Dimethylfulvene 1.8 mL (14.7 mmol) was added to (1.5.7-

triaza[4.4.0]bicyclo-dec-5-enyl) potassium 2.6g (14.7

mmol) in THF at 0°C over one hour. The mixture was

stirred at ambient temperature overnight, and the

solvent removed under vacuum. The product was washed

30   with pentane and dried under vacuum to afford 3.2g

(79.05%) of light grey solid. ^{1}H-NMR in THF δ:5.92 (dd,

2H), 5.65 (dd, 2H), 3.10 (t, 4H), 3.04 (t, 4H), 3.81 (s,

6H), 3.61 (m, 4H). ^{13}C-NMR in THF δ:151.0, 142.4, 121.9,

105.8, 102.9, 48.2, 41.8, 23.6, 22.2. MS analysis

35   showed the decomposition pattern of the parent title

compound. No M^+ was detected due to the decomposition of

the sample during the analysis. Elemental analysis

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calculated C 63.56% H 7.82% N 14.82% K 13.79%, found C
63.36% H 7.75% N 15.07% K 13.55%.

Example 23

Dimethylmethylene cyclopentadienyl triazabicyclodec-ene-
yl-1 chromium dichloride $C_{15}H_{22}Cl_2CrN_3$.
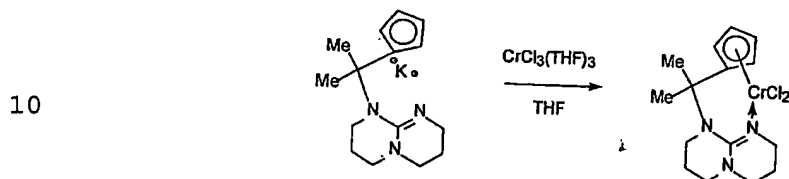
Dimethylmethylene cyclopentadienyl triazabicyclodec-ene-
yl-1 potassium $CrCl_3(THF)_3$ 3.4 g (9.08 mmol) in THF was
added to a solutiuon of triazabicyclodec-ene-yl-1-
dimethyl-methylene potassium 2.6 g (9.08 mmol) in THF at
-30^0C over a period of 30 minutes. The mixture was
stirred overnight at ambient temperature. Solvent was
removed under reduced pressure and the product extracted
in toluene, filtrated and dried under vacuum. The
filtrate was then extracted in dichloromethane,
filtrated, and dried again under vacuum. The product
was washed with pentane to afford pure dark blue
microcrystalline solid 2.3 g (68.7%). EIMS analysis
showed the decomposition pattern of the title compound,
$M^+=367.26$ g mol^{-1} peak was not detected due to
decomposition during analysis. Elemental analysis
calculated C 49.06% H 6.04% N 11.44% Cl 19.31% Cr
14.16%, found C 47.81% H 6.06% N 13.05% Cl 18.80% Cr
13.60%.

Polymerization examples

Table 1 - Ethylene homopolymerization test results using
homogeneous catalysts

Complex	Act. HOPO	M_w x10^3	M_w/M_n	Cryst. %	m.p. °C	Al/M
Example 6 Me$_2$Si(Me$_2$Cp-OSiMe$_2$-tBu)(TAB)CrCl$_2$	2778	n.d.	n.d.	53.6	134.3	757
Example 8 Me$_2$Si(Cp-OSi-iPr$_3$)(TAB)CrCl$_2$	395	977	30.2	57.1	135.1	778
Example 13 Ph$_2$Si(Me$_4$Cp)(TAB)CrCl$_2$	1048	412	27.8	66.7	133.2	1000
Example 10 Me$_2$Si(Flu)(TAB)CrCl$_2$	50	272	6.6	58.9	134.2	1000

[1] Al/M ratio 700-1000, MAO, temp+60°C, C$_2$= 10 bar. n.d. = not determined (too high M$_w$ for GPC measurement device). Activity in [kg PE/g met, h^{-1}]

Table 2 - Ethylene homopolymerization using homogeneous catalysts and hydrogen

Complex	Act. HOPO/H$_2$	M_w x10^3	M_w/M_n	Cryst. %	m.p. °C	Al/M
Example 6 Me$_2$Si(Me$_2$Cp-OSiMe$_2$-tBu)(TAB)CrCl$_2$	1902[1]	198	7.4	71.1	132.5	1000
Example 13 Ph$_2$Si(Me$_4$Cp)(TAB)CrCl$_2$	2628.1	-	-	-	-	-
Example 8 Me$_2$Si(Cp-OSi-iPr$_3$)(TAB)CrCl$_2$	486	192	8.1	67.3	135.7	763

[1] Amount of hydrogen fed to the 2 L reactor was 0.6 bar/677 mL [2] Amount of hydrogen fed to the 2 L reactor was 0.3 bar/677 mL. n.d. = not determined (too high M$_w$ for GPC measurement device). Activity in [kg PE/g met. h^{-1}]. Temp. +60°C.

Table 3 - Copolymerization of ethylene and 1-hexene using homogeneous catalysts

Complex	Act. COPO
Example 13 Ph$_2$Si(Me$_4$Cp)(TAB)CrCl$_2$	2713.5
Example 23 Me$_2$C(Cp)(TAB)CrCl$_2$	91.62

Activity in [kg PE/g met. h^{-1}]

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Table 4 - Polymer double bond analysis results of the
ethylene homopolymers[#]

Complex	t-vinylene	vinyl	vinylidene
Example 6 $Me_2Si(Me_2Cp-OSiMe_2-tBu)(TAB)CrCl_2$	0.11	0.09	0.03
Example 8 $Me_2Si(Cp-OSi-iPr_3)(TAB)CrCl_2$	n.d.	n.d.	n.d.
Example 13 $Ph_2Si(Me_4Cp)(TAB)CrCl_2$	0.21	0.71	0.12
Example 10 $Me_2Si(Flu)(TAB)CrCl_2$	0	0.18	0.05

Unit is double bonds per 1000 carbon atoms (C=C/1000C).

Table 5. Propylene polymerisations. Al/Cr ratio 1000,
polymerisation time 90 minutes. 5 bar propylene pressure
(60°C). Cocatalyst MAO & TIBA (tetraisobutylalumoxane)
150µL, 1100 g propylene.

Complex	Yield of Polymer	Notes
Example 6	0.7 g	
Example 6	1.4	6 g Ethylene added

Table 6. Analysis results of the polymers

Code	Run Type	DSC (%)	DSC, TCR1 (°C)	TM1 (°C)	MN (g/mol)	MW (g/mol)	MW/MN	MZ (g/mol)	MFR21	T-VINYL	VINYL	VINYLIDEN
8	HOPO60	57.1	115.9	135.1	32300	977000	30.2	6302000	0.03			
8	HOPO80	64	116.2	129.9					not done	0.16	1.46	0.6
8	HOPO/H260	67.3	116.3	135.7	23600	192000	8.1	1192000	14.5	0	0.27	0.1
6	HOPO60	53.6	115.9	134.3					0.008	0.11	0.09	0.0
6	HOPO80	72.3	118.2	131.3					28.4	0.84	0.68	0.2
6	HOPO/H260	71.1	119	132.5	26900	198000	7.4	3553000	42.5	0.06	0.09	0.0

Heterogeneous polymerisation test result of compound 20 using silica

Pol type	Activity of cat (KgPol/g cat h)	Activity of metal KgPol/g met h	Al/Me	Flowmeter C2 (g)	Temperature (°C)	DSC CR1 (%)	TCR1 (°C)	TM1 (°C)
HDPE	0.01	4.6	200	28	60	49.1	119.9	113.4
HDPE	0.00	4.3	200	24	80	51.3	120	132.5

MN1	GPC-Normal MW1	MW1/MN1	MZ1	MFR 21.6KG	FTIR, (C=C/1000C) T-VINYLENE	VINYL	VINYLIDENE
204600	1899000	9.3	6079000	not done	X	X	X
19000	1742000	91.7	9030000	not done	X	X	X

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Claims

1.   A compound of formula (I)

(I)

wherein

LIG represents an η^5-ligand substituted by a group R_1 and a group $(R'')_m$;

X represents a 1 to 3 atom bridge;

Y represents a nitrogen or phosphorus atom;

Z represents a carbon, silicon, nitrogen or phosphorus atom;

the ring denoted by A_1 is an optionally substituted, optionally saturated or unsaturated 5 to 12 membered heterocyclic ring;

the ring denoted by A_2 is an optionally substituted, unsaturated 5 to 12 membered heterocyclic ring;

R_1 represents hydrogen, R'' or a group $OSiR'_3$;

each R', which may be the same or different is a R^+, OR^+, SR^+, NR^+_2 or PR^+_2 group where each R^+ is a C_{1-16} hydrocarbyl group, a tri-C_{1-8}hydrocarbylsilyl group or a tri-C_{1-8}hydrocarbylsiloxy group;

each R'', which may be the same or different is a ring substituent which does not form a σ-bond to a metal η-bonded by the bicyclic ring; and

m is zero or an integer between 1 and 3.

2.   A compound as claimed in claim 1 wherein Z represents a nitrogen atom.

3.   A compound as claimed in claim 1 or 2 wherein Y represents a nitrogen atom.

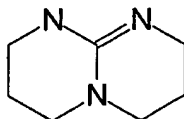4.   A compound as claimed in any one of claims 1 to 3

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wherein A_1 and A_2 are five or six-membered rings.

5.   A compound as claimed in any one of claims 1 to 4 wherein A_1 and A_2 are unsubstituted and comprise only 1 double bond.

6.   A compound as claimed in any one of claims 1 to 5 wherein A_1 and A_2 represent

7.   A compound as claimed in any one of claims 1 to 6 wherein LIG comprises a dipyridymethanyl, cyclopentadienyl, fluorenyl or indenyl ligand.

8.   A compound as claimed in any one of claims 1 to 7 wherein R" represents hydrogen, R^+, OR^+, SR^+, NR^+_2 or PR^+_2 group where each R^+ is a C_{1-16} hydrocarbyl group, a tri-C_{1-8} hydrocarbylsilyl group or a tri-C_{1-8}hydrocarbylsiloxy group.

9.   A compound as claimed in any one of claims 7 or 8 wherein LIG represents cyclopentadienyl and R_1 represents $OSiR'_3$ each R' being a C_{1-12} hydrocarbyl group.

10.   A compound as claimed in claim 9 wherein R" represents C_{1-6} alkyl.

11.   A compound as claimed in claim 1 wherein LIG represents

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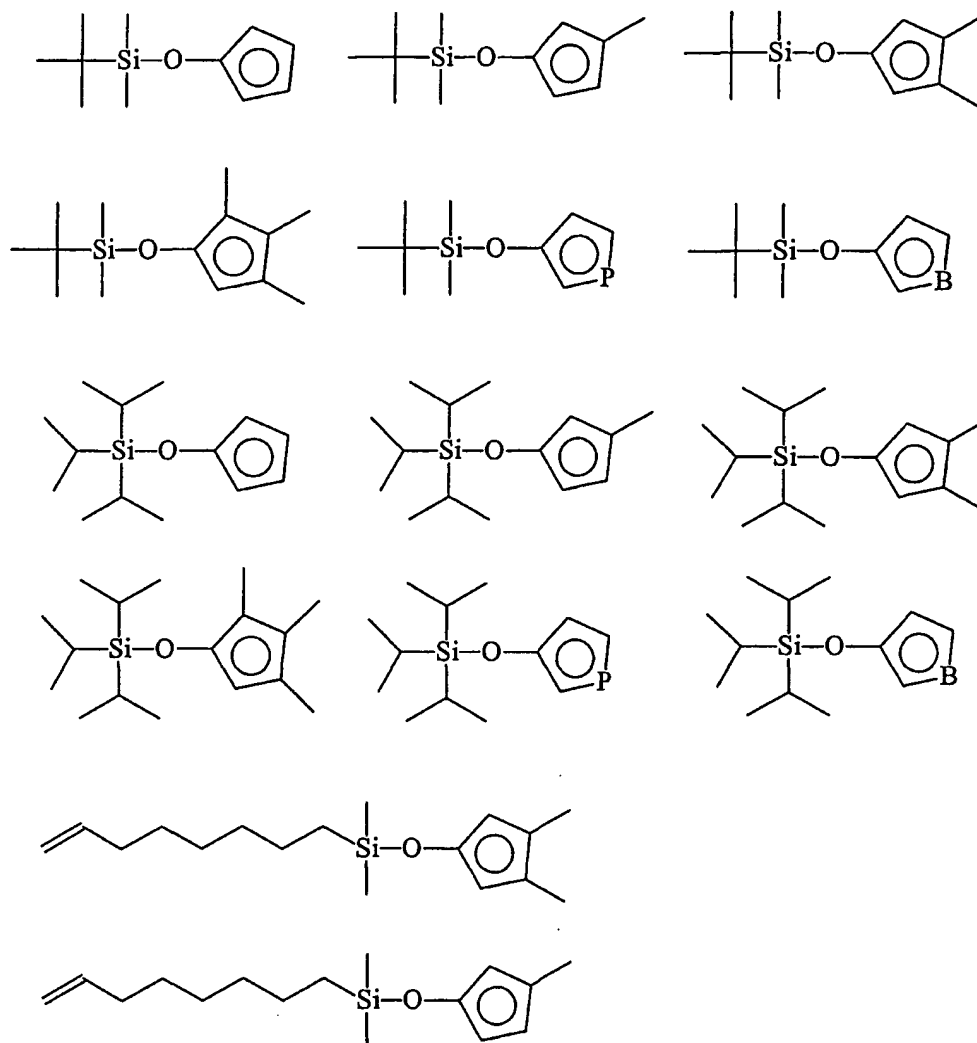
12. A compound as claimed in any one of claims 1 to 10 wherein m is 3, LIG is a cyclopentadienyl and R" is methyl.

5

13. A compound as claimed in any one of claims 1 to 12 wherein X is a one atom bridge comprising Si or a one atom bridge comprising a carbon atom.

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14. A compound as claimed in any one of claims 1 to 7

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wherein LIG represents fluorenyl, indenyl or
dipyridymethanyl and R' and R" represent hydrogen.

5   15. A compound as claimed in any one of claims 1 to 13
of formula
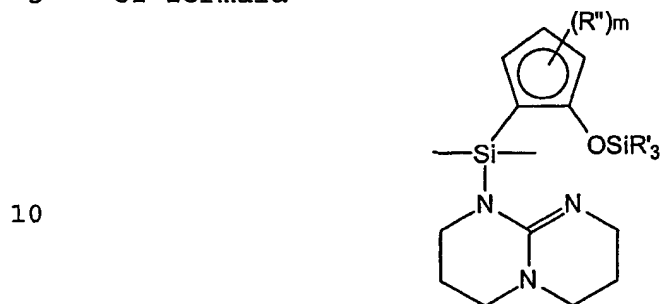
wherein R', m and R" are as hereinbefore defined.

16. A procatalyst comprising a compound of formula (I)
as claimed in any one of claims 1 to 11 coordinated to a
metal ion of group 3 to 7, the Y atom not being
coordinated to the metal.

17. A procatalyst as claimed in claim 16 wherein said
metal ion is an ion of Cr or Ti.

18. A procatalyst as claimed in claim 16 or 17 wherein
said metal is additionally coordinated to a halogen σ-
ligand.

19. A procatalyst as claimed in any one of claims 16 to
18 wherein at least one of the atoms N or Z or the
double bond of the bicyclic ring is coordinated to the
metal ion.

20. A procatalyst as claimed in claim 19 wherein the
group LIG and the atom N are coordinated to the metal
ion.

21. An olefin polymerisation catalyst system comprising

or produced by reaction of (1) a procatalyst as claimed
in claims 16 to 20 and (2) a cocatalyst.

22.   A process for olefin polymerisation comprising
polymerising an olefin in the presence of a catalyst
system as described in claim 21.

23.   A process for the preparation of a procatalyst,
said process comprising metallating with a group 3 to 7
transition metal a compound of formula (I)

wherein LIG, X, Y, Z and rings A_1 and A_2 are as
hereinbefore defined.

24.   The use of a procatalyst as claimed in any one of
claims 16 to 20 in olefin polymerisation.

25.   An olefin polymer produced by a polymerisation
catalysed by a procatalyst compound as claimed in any
one of claims 16 to 20.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7   C07F7/18   C07F17/00   C08F10/00   C08F4/69

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C07F   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 40420 A (EASTMAN CHEMICAL CO., USA) 17 September 1998 (1998-09-17) page 65 ---	1-25
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; CHEN, SHI-CHOW: "The syntheses and mass spectra of some N-substituted ferrocenylmethyl adenines" retrieved from STN Database accession no. 94:121682 XP002181981 abstract & J. ORGANOMET. CHEM. (1980), 202(2), 183-9 , ---	1

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X	Further documents are listed in the continuation of box C.		X	Patent family members are listed in annex.

° Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 November 2001	21/11/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340-2040, Tx. 31 651 epo nl, Fax: (+31–70) 340-3016	Bader, K

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HOULTON, ANDREW ET AL: "Synthesis, structure and redox properties of ferrocenylmethylnucleobases" retrieved from STN Database accession no. 132:3427 XP002181982 abstract & J. CHEM. SOC., DALTON TRANS. (1999), (18), 3229-3234 ,	1
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; NEKRASOV, YU. S. ET AL: "Ferrocenylalkylation of nucleic acid bases" retrieved from STN Database accession no. 128:192751 XP002181983 abstract & ROSS. KHIM. ZH. (1997), 41(4), 117-120 ,	1
E	WO 01 70395 A (ANDELL OVE ;KETOLA LASSE (FI); MAARANEN JANNE (FI); BOREALIS TECH) 27 September 2001 (2001-09-27) page 20 -page 24	1-8,14, 16-25

FURTHER INFORMATION CONTINUED FROM   PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-14,16-25 (all partially not searched)

Present claims relate to an extremely large number of possible compounds.
In fact, the claims contain so many options, variables, possible
permutations and provisos that a lack of clarity and conciseness within
the meaning of Article 6 PCT arises to such an extent as to render a
meaningful search of the claims impossible. Consequently, the search has
been carried out for those parts of the application which do appear to be
clear and concise, namely compounds according to claim 1 wherein the LIG
moiety is selected from the list of claim 7 and wherein A1 and A2 are
unsubstituted ringsystems, which comprise only one double bond as
described in claim 5. (combined teaching of claims 5 and 7)

Also the claims 16-25 have been searched under the aforementioned
restrictions only.

The applicant's attention is drawn to the fact that claims, or parts of
claims, relating to inventions in respect of which no international
search report has been established need not be the subject of an
international preliminary examination (Rule 66.1(e) PCT). The applicant
is advised that the EPO policy when acting as an International
Preliminary Examining Authority is normally not to carry out a
preliminary examination on matter which has not been searched. This is
the case irrespective of whether or not the claims are amended following
receipt of the search report or during any Chapter II procedure.

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9840420	A	17-09-1998	EP	0966490 A2	29-12-1999
			WO	9840420 A2	17-09-1998
			US	6200925 B1	13-03-2001
			US	2001025007 A1	27-09-2001
			CN	1258292 T	28-06-2000
			EP	0975682 A1	02-02-2000
			EP	0973762 A2	26-01-2000
			WO	9847933 A1	29-10-1998
			WO	9840374 A2	17-09-1998
			US	6103658 A	15-08-2000
			US	6245871 B1	12-06-2001
			US	6303720 B1	16-10-2001
			US	2001014646 A1	16-08-2001
WO 0170395	A	27-09-2001	WO	0170395 A2	27-09-2001